PORTLAND CEMENT

Its Composition, Raw Materials, Manufacture, Testing and Analysis

BY

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PREFACE.

The present treatise upon Portland cement is really the second edition of a small manual by the writer, published some four years ago, called "The Chemical and Physical Examination of Portland Cement." In preparing this new edition, it seemed wise to add a section on the manufacture of Portland cement, for the reason that the chemist who is to intelligently supervise the process of manufacture, as well as the chemist who is to report upon the raw materials and the engineer who is to inspect the product, should have a good, general knowledge of the technology of Portland cement.

It was also found necessary to rewrite almost the entire section upon the physical testing of cement in order to give special prominence to the uniform methods of testing adopted by the American Society of Civil Engineers, and to the standard specifications of the American Society for Testing Materials. Much new matter has also been added to the section on the analysis of cement and its raw materials, and sections on the experimental manufacture of small lots of cement and on the history of the industry have been included.

The analytical methods have all been used to some extent in the writer's laboratory and have been found satisfactory. Comments as to their accuracy and advice as to the best methods of manipulation will usually be found with each method under the heading, "notes."

The author again wishes to thank the many friends who have aided him in the preparation of both this and the former edition.

NAZARETH, PA., July, 1906.

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INTRODUCTION.

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The Beginning of the Industry in England.

The cement industry proper dates from the researches of an English engineer, John Smeaton, who had been employed by parliament to build a lighthouse upon a group of gneiss rocks, in the English Channel, just off the coast of Cornwall. These crags, known as Eddystone, were at high tide under water for some hours and many shipwrecks had occurred upon them. They were a menace to the navigation of this part of the channel and it was necessary to warn sailors of their whereabouts. Two wooden structures built upon them had been subjected to the fury of the elements and had each experienced but a short life.

When Smeaton attacked the problem, he determined to build a structure which would weather the fiercest storms of the channel and would come out of these an enduring monument to his engineering skill. One of the greatest difficulties he had to overcome was the failure of ordinary lime mortar (the discovery of which dates back to antiquity) to harden under water. In order that his foundations should be firm, it was necessary that some mortar be found which would meet this difficutly. To this end he undertook a series of investigations in 1756, the result of which was the discovery that the hard, white, pure limestones, hitherto considered best for lime making, were in reality inferior to the soft clayey ones[1]; for from these latter he succeeded in obtaining a lime far superior to any then in use because it not only hardened better in air, but would also harden under water. Such a limestone Smeaton found near at hand, at Aberthaw, in Corn-

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[1] Smeaton—Narrative of the building, etc., of the Eddystone Lighthouse, Book IV.

wall, and the hydraulic lime formed by burning this stone was the basis of the mortar used in the construction of the Eddystone lighthouse.

Smeaton in making his hydraulic lime, however, used only those layers of his quarry which after burning gave a product that would slake with water. The idea of burning the layers which would not slake readily and then by grinding, convert them into a very energetic hydraulic lime did not suggest itself to him and it was not until forty years later that this first improvement was made in the manufacture of hydraulic lime. In 1796, one Joseph Parker, of Northfleet, in Kent Co., Eng., took out a patent for the manufacture of a hydraulic lime which he called "Roman Cement" and which he made by calcining or burning the argillo-calcarious, kidney-shaped nodules called "septaria" and then grinding the resulting product to a powder.[1] In composition these nodules were very similar to what we now call Rosendale cement rock. They occurred geologically in the London clay formation and were usually obtained from the shores of the Isle of Sheppy where they were washed up after a storm. This cement came rapidly into favor with the English engineers because much work could be done with it that was impossible with quick lime. In 1802 cement was produced from the same "septaria" at Boulogne, France, and this was the beginning of the cement industry in that country.

In 1810, Edgar Dobbs, of Southwick, England, obtained a patent for the manufacture of an artificial Roman cement by mixing carbonate of lime and clay, in suitable proportions, moistening, molding into bricks, and burning sufficiently to expel the carbonic acid, without vitrifying the mixture. Soon after this, General Sir Wm. Paisley, in England, and L. J. Vicat, a French engineer, both independently of each other, made exhaustive experiments looking to the manufacture of an artificial Roman cement by mixing clay with chalk, etc. In 1813 Vicat began the manufacture of artificial hydraulic cement in France, as did also James Frost in England, in 1822.

Invention of Portland Cement.

In 1824, Joseph Aspdin, a bricklayer of Leeds, England, took

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[1] Redgrave—Calcareous Cements.

out a patent on an improved cement which he proposed to make from the dust of roads repaired with limestone, or else from limestone itself combined with clay, by burning and grinding. This cement he called "Portland Cement," because when hardened it produced a yellowish gray mass resembling in appearance the stone from the famous quarries of Portland, England.

At this point, it seems proper to state that there are now manufactured and sold in this country three kinds of hydraulic cement:

First—Natural, Natural Rock, Rosendale, or Roman cement, which is made by burning suitable clayey limestones to the point when most of the carbonic acid is expelled and then grinding to a powder the resulting soft brownish yellow clinker.

Second—Portland cement which is made by grinding to an impalpable powder a mixture of argillaceous and calcareous substances in proper proportions, burning the mixture to the point of incipient vitrifaction and then regrinding the resulting greenish black clinker.

Finally—Slag or Puzzolan cement which is made by grinding together without subsequent calcination a mixture of blast furnace slag and slaked lime. It is now generally accepted that the cements used by the Romans were of this character and were made from volcanic slag called "Puzzolana" (from the town Puzzuoli, at the foot of Mt. Vesuvius, where its properties were first discovered). It is supposed that the Romans mixed this slag with slaked-lime and a small amount of sand for their hydraulic mortar. There are authorities, Cummings among them, who contend that the Romans knew how to make Rosendale or Natural cement and that their concrete work was done with this.[1]

Aspdin is usually credited with the invention of Portland cement and while he certainly did originate the name "Portland Cement" he probably did nothing more than make an artificial Roman cement, which had been done before, since he apparently did not carry his burning to the point of incipient vitrifaction, which we now recognize as being an essential point in the manufacture of Portland cement.[2] Aspdin erected a factory at Wakefield, England, for the manufacture of his cement, which

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[1] Cummings—American Cements.

[2] Michaelis—Thonindustrie Zeitung, Jan. 16, 1904.

was used upon the Thames Tunnel in 1828. At first Portland cement was sold at prices considerably lower than the Natural or Roman cement of Parker and his successors, and it was not until John Grant, in 1859, decided to use Portland cement in the construction of the London drainage canal, of which he was chief engineer, and published his reasons for doing so in the transactions of the Institution of Civil Engineers, that the new cement began to come to the front.

It is evident that by this time the value of burning the clinker to the point of incipient vitrifaction had been discovered and made use of—probably first in the famous old works of White & Bros., established by James Frost at Swanscombe, in 1825, and still existent. In 1852 the first German Portland cement works were established near Stettin. The Germans were quick to see the value of the new building material, and with their fine technologists soon turned out a better product, by the substitution of scientific methods in place of rules of thumb. They were the first to appreciate the value of fine grinding of the cement, and until recently the German Portlands were the standard. Today probably the best Portland cement made in the world is turned out in America.

Discovery of Cement Rock in the United States.

In this country the cement industry began with the discovery in 1818, of a natural cement rock near Chittenango, Madison Co., N. Y., by Mr. Canvass White, an engineer engaged in the construction of the Erie canal, who after some experimenting applied to the State of New York for the exclusive right to manufacture this cement for twenty years. The state denied his request but gave him $20,000 in recognition of his valuable discovery.[1] His cement was used in large quantities in the construction of the Erie canal and brought a price of about twenty cents a bushel.

As the greatest users of cement in this country were the canals, and as they at that time furnished the only means for the transportation of bulky materials, there was naturally the sharpest lookout kept along their line of construction for limestone suit-

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[1] Sylvester—History of Ulster County, N. Y.

able for the making of hydraulic cement. In consequence of this, nearly all the early cement mills were started along the line of, and to furnish cement for, the construction of some canal. In 1825, cement rock was discovered in Ulster County, New York, along the line of the Delaware and Hudson canal and in the following year a mill was started at High Falls in that county. In 1828, a mill was built at Rosendale, also in Ulster County. This soon became the center of the industry and the cement made here was called Rosendale. This name is still largely applied to American natural cements. The first cement was made in small upright kilns. Wood was used as fuel and the burning continued for about a week. The clinker was then ground between mill stones by water power. After these mills had been in operation several years continuous kilns were introduced which permitted the clinker to be drawn daily, coal being used as fuel.

In 1829 cement rock was discovered near Louisville, Ky., while constructing the Louisville & Portland Canal, and John Hulme & Co. almost immediately began the manufacture of Louisville cement at Shippingport, a suburb of Louisville.[1]

During the construction of the Chesapeake and Ohio Canal, cement rock was discovered, in 1836, in Maryland, at Round Top, near Hancock, and it has been manufactured there ever since. Other canals along whose lines cement rock was discovered with the location and date, are the Illinois and Michigan Canal, at Utica, in 1838; James River Canal, at Balcony Falls, Va., in 1848; and Lehigh Coal and Navigation Co. Canal, at Siegfried, Pa., in 1850. At all of these points the manufacture of cement has been continuous. Other well known brands of cement began to be manufactured as follows: Akron, N. Y., 1840; Ft. Scott, Kan., 1868; Buffalo, N. Y., 1874; and Milwaukee, Wis., in 1875.

The process for making natural cement is in general as follows: The rock is blasted down from the face of the quarry, broken by hand with sledges into sizes suitable for the kiln, loaded on dump cars and elevated to the mouth of the kilns. Here the rock is dumped into the kiln alternately with coal, a layer of rock and then a layer of coal. The charging is kept up continuously during the daytime but hardly ever at night. As the charge works

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[1] Lesley—Jour. Assoc. Eng. Socs., Vol. XV., p. 198.

its way down through the kiln it becomes calcined and the larger portion of its carbonic acid driven off. When it reaches the base of the kiln it is drawn out and conveyed to the grinding machinery. The kilns used for the manufacture of natural cement are usually made of iron plates riveted together and lined with fire brick. They are circular in shape, upright, and their average dimensions are about 16 feet in diameter by 45 feet in height.

The clinker is usually ground by buhr-stones, the fine material in many mills being separated from the coarse by passing over screens, so placed as to allow the fine particles to go to the storehouse and to return the coarse ones to the grinders. The buhrstones are preceeded by crushers or crackers to reduce the clinker to a suitable size for them to handle. In some instances ball and tube mills and Griffin mills have been installed in natural cement plants, particularly where these plants also make Portland, but the clinker from these kilns is usually so soft as to be easily ground by buhr-stones.

There are now in this country between 60 and 70 mills manufacturing natural cement. Below are some figures on the production of natural cement in this country.

TABLE I.—PRODUCTION OF NATURAL CEMENT IN UNITED STATES, 1818–1904.
(Mineral Resources of the United States, 1904.)

Year.	Barrels.	Year.	Barrels.	Year.	Barrels.
1818 to 1830	300,000	1885	4,100,000	1896	7,970,450
1830 to 1840	1,000,000	1886	4,186,152	1897	8,311,688
1840 to 1850	4,250,000	1887	6,692,744	1898	8,418,924
1850 to 1860	11,000,000	1888	6,253,295	1899	9,868,179
1860 to 1870	16,420,000	1889	6,531,876	1900	8,383,519
1870 to 1880	22,000,000	1890	7,082,204	1901	7,084,823
1880	2,030,000	1891	7,451,535	1902	8,044,305
1881	2,440,000	1892	8,211,181	1903	7,030,271
1882	3,165,000	1893	7,411,815	1904	4,866,331
1883	4,190,000	1894	7,563,488		
1884	4,000,000	1895	7,741,077		

TABLE II.—PRODUCTION OF NATURAL ROCK CEMENT IN 1902, 1903 AND 1904 BY STATES.

(From Mineral Resources of United States, 1904.)

State.	1902. *a*			1903. *b*			1904. *c*		
	Number of works.	Quantity.	Value.	Number of works.	Quantity.	Value.	Number of works.	Quantity.	Value.
		Barrels.			*Barrels.*			*Barrels.*	
Georgia	2	55,535	$ 31,444	2	80,620	$ 44,402	2	66,500	$ 37,750
Illinois	3	607,820	156,855	3	543,132	178,900	3	360,308	113,000
Indiana	....	....	....	....	....	....	13	735,906	367,953
Kentucky	15	1,727,146	869,163	15	1,533,573	766,786	2	264,104	132,052
Kansas	2	160,000	80,000	2	226,293	169,155	2	210,922	79,456
Maryland	4	409,200	150,680	4	269,957	138,619	4	65,000	32,500
Minnesota	2	150,000	67,500	2	175,000	78,750	2	138,000	65,620
Nebraska	....	....	....	....	....	....	1	....	....
New York	19	3,577,340	2,135,036	20	2,417,137	1,510,529	19	1,911,402	1,138,667
North Dakota	1	....	....	1	....	....	1	....	....
Ohio	2	....	....	2	67,025	46,776	1	....	....
Pennsylvania	6	796,876	340,669	7	1,339,090	576,269	5	770,897	298,533
Texas	1	....	....	2	....	....	1	....	....
Virginia	2	34,000	20,000	2	47,922	25,961	2	93,292	59,619
West Virginia	1	88,475	62,655	1	....	....	1	....	....
Wisconsin	2	437,913	162,628	2	330,522	139,373	2	250,000	125,000
Total	62	8,044,305	4,076,630	65	7,030,271	3,675,520	61	4,866,331	2,450,150

a The production of North Dakota, Ohio and Texas is combined with that of West Virginia, and the production of Indiana with that of Kentucky.

b The production of North Dakota and Texas is combined with that of Kansas, and the production of Indiana with that of Kentucky.

c The production of North Dakota is combined with Minnesota, Ohio with Virginia, and Texas with Kansas.

It will be noticed that there is little increase in the production of natural cement since 1890. This is due to the fact that since that time Portland cement has been fast displacing natural cement. The increase in production in 1900 was due to the strong demand for building materials that year; a demand that could not be supplied by the Portland cement manufacturers. Our imports in 1900 were over 3,000,000 barrels of Portland, in spite of the fact that the home mills produced over 3,000,000 barrels more than in 1899.

Beginning of the Portland Cement Industry in the United States.

As we have stated cement rock was discovered in 1850 at Siegfried, in Northampton Co., Pa., on the line of the Lehigh Coal and Navigation Co.'s canal leading from Easton to Mauch Chunk. As the cement for the canal had to be brought from New York, the discovery was a valuable one and was put to immediate use by the erection of a mill at Siegfried.

In the spring of 1866, Messrs. David O. Saylor, Esaias Rehrig and Adam Woolever, three gentlemen, of Allentown, Pa., formed the Coplay Cement Co., and located a mill at Coplay, near Allentown, and not far from Siegfried. Mr. Saylor was president and superintendent of the company. The plant made excellent cement though its methods for doing so were crude. Early in the seventies Mr. Saylor began to experiment upon the manufacture of Portland cement from the rocks of his quarry. No Portland cement was made in this country then, and most of it in use here came from England and Germany. Its reputation was established and it was looked upon as superior to Rosendale cement.

Mr. Saylor was led to make his experiments by the fact that he noticed the harder burned portions of his Rosendale clinker gave a cement which for a short period would show a tensile strength equal to that of the best imported Portland; but he found this cement would crumble away with time. This was due to the raw materials not being properly proportioned. The result of these experiments taught him that if he mixed a certain amount of cement rock high in lime with his ordinary cement rock he could make Portland cement, and after many trial lots were burned the company turned out its first Portland in 1875. This was the first

Portland cement made in the Lehigh District, and it was made from a material totally different from that used in any of the European mills.

The drawings for the first kilns were made by James Cabott Arch, an English engineer, and were bottle-shaped.

Having solved the problem of how to make Portland cement, Saylor found another and equally difficult one awaiting him of how to sell it, after it was made. The labor cost of manufacturing his cement was great and he could not afford to offer it at prices much below the imported article. As the foreign cements had an established record, they fought the new cement with the argument that any brand of Portland cement required time to prove itself, and it was only by liberal advertising and an iron-clad guarantee of his product that Saylor secured a market.

Among the first great engineering works upon whose construction Saylor's Portland cement was used were the Eads jetties along the Mississippi River, and the first great sky-scraper in which American Portland cement was used was the Drexel Building in Philadelphia. Slowly American Portland cement overcame the prejudice against it and it is now recognized as superior to that manufactured in any part of the world. Saylor's original plant turned out only 1,700 barrels of Portland cement a year. Since its inception, however, it has grown steadily and now has a capacity of considerably over this amount a day.

Development in Other States.

While Saylor was conducting his experiments in the Lehigh Valley, a Chicago concern, known as the Eagle Portland Cement Co., built a plant near Kalamazoo, Mich., about 1872, to manufacture Portland cement from marl and clay. This plant at first consisted of two bottle-shaped kilns, which number was afterwards increased to four. The product was known as "Eagle Portland Cement," and its quality must have been excellent as some three of four miles of sidewalk put down in Kalamazoo are still in good condition. This mill, however, was forced to shut down in 1882, for although its product sold at from $4 to $4.25 per barrel, it could not manufacture cement at a figure below this. Today no traces of even the kilns remain.[1]

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[1] Russell—Twenty-second Annual Report, U. S. Geological Survey, Part III.

At Wampum, Pa., a small plant was started to make cement from limestone and clay, in 1875. Thomas Millen found, at South Bend, Ind., a white marl and clay which resembled in composition, the material used for cement making in England, and started a small plant there in 1877.[2] Both the plants at Wampum and South Bend, Ind., are now producers, though in a modest way. In Maine also a small plant was started by the Cobb Lime Co., at Rockport, in 1879, but this too failed to make cement at a figure below its selling price and closed down permanently as did also a small plant in the Rosendale district started about the same time.

Of the six works started prior to 1881 half that number were failures and represented a complete loss to their promoters. The cement made at Coplay and Wampum, however, was on exhibition at the Philadelphia Centennial in 1876, and held its own with the imported article.

About 1883, a small plant for the manufacture of Portland cement was inaugurated at Egypt, Pa., near Coplay, by Robt. W. Lesley, the first president of the recently formed American Association of Portland Cement Manufacturers, John W. Eckert, Saylor's first chemist, and others. This plant progressed gradually and developed into the American Cement Co., now a large producer of both natural and Portland cecent. From this time on plants sprung up rapidly in the Lehigh Valley Section, among the older ones being the Atlas, Bonneville, Alpha and Lawrence, all now important producers.

In other sections also, successful mills were built.. In New York, Thomas Millen, who had previously built a works in Indiana, and his son, Duane Millen, started the Empire Portland Cement Co., at Warners, Onondaga Co., in 1886. In Ohio, at Harper, Logan Co., the Buckeye Portland Cement Co. put in operation their plant in 1889; and in 1890 the Western Portland Cement Co., of Yankton, S. D., began to make Portland cement.

From that time on the Portland cement industry has taken rapid strides and plants have been built in almost every part of the country. The process of manufacture has been greatly improved, resulting in a considerable lessening of the cost of production.

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[1] Cement Age, July, 1905, contains an interesting account by Mr. Millen himself of how he came to go into the manufacture of Portland cement at South Bend.

American Portland cement has practically displaced the imported article. New uses have been found for Portland cement and it is coming rapidly to the front as a material of construction. The new American Association of Portland Cement Manufacturers formed in 1902, promises to do wonders for the industry and to the end of showing the many uses to which Portland may be applied with advantage, erected a building and prepared an exhibit for the Louisiana Purchase Exposition at St. Louis during 1904.

Tables III, IV and V show the growth of the American Portland Cement industry and Table VI gives a graphic comparison of the imports, production and consumption of Portland and Natural cements from 1890 to 1903.

TABLE III.—TOTAL PRODUCTION OF PORTLAND CEMENT IN THE UNITED STATES, 1870 TO 1904.

(Mineral Resources of United States.)

Year.	Barrels.	Year.	Barrels.	Year.	Barrels.
1870 to 1880	82,000	1888	250,000	1896	1,543,023
1880	42,000	1889	300,000	1897	2,677,775
1881	60,000	1890	335,000	1898	3,692,284
1882	85,000	1891	454,813	1899	5,652,266
1883	90,000	1892	547,440	1900	8,482,020
1884	100,000	1893	590,652	1901	12,711,225
1885	150,000	1894	798,757	1902	17,230,644
1886	150,000	1895	990,324	1903	22,342,973
1887	250,000			1904	26,505,881

TABLE IV.—PRODUCTION OF PORTLAND CEMENT IN THE UNITED STATES IN 1902, 1903 AND 1904, BY STATES.

(Mineral Resources of United States, 1904.)

State.	1902. *a*			1903. *b*			1904. c		
	Number of works.	Quantity.	Value.	Number of works.	Quantity.	Value.	Number of works.	Quantity.	Value.
		Barrels.			*Barrels.*			*Barrels.*	
Alabama	1	......	......	1	......	......	1	......	......
Arkansas	1	......	......	1	......	......	1	......	......
California	2	294,156	$ 431,910	3	631,151	$ 1,019,352	3	1,014,558	$ 1,446,909
Colorado	2	82,044	105,016	1	258,773	436,535	1	490,294	638,167
Georgia	1	......	......	2	......	......	2	......	......
Illinois	4	767,781	977,541	5	1,257,500	1,914,500	5	1,326,794	1,449,114
Indiana	3	536,706	628,244	3	1,077,137	1,347,797	4	1,350,797	1,232,071
Kansas	1	830,050	1,017,824	1	1,019,682	1,285,310	2	2,643,939	2,134,612
Kentucky	......	......	......	......	......	......	1	......	......
Michigan	10	1,577,006	2,134,396	13	1,955,183	2,674,780	16	2,247,160	2,365,656
Missouri	1	......	......	2	825,257	1,164,834	2	......	......
New Jersey	2	2,152,158	2,563,355	3	2,693,381	2,944,604	3	2,799,419	2,099,564
New York	10	1,156,807	1,521,553	12	1,602,946	2,031,310	12	1,362,514	1,257,561
Ohio	7	563,113	685,571	8	729,519	998,300	7	910,297	987,899
Pennsylvania	15	8,770,454	10,130,432	17	9,754,313	11,205,892	17	11,496,099	8,969,206
South Dakota	1	......	......	1	......	......	1	......	......
Texas	2	165,500	234,950	2	......	......	2	......	......
Utah	1	......	......	1	......	......	1	......	......
Virginia	1	334,869	433,286	1	538,131	690,105	1	864,093	774,360
West Virginia	......	......	......	1	......	......	1	......	......
Total	65	17,230,644	$20,864,078	78	22,342,973	$27,713,319	83	26,505,881	23,355,119

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a The production of Alabama and Georgia is combined with Virginia, the production of Missouri and South Dakota with that of Kansas, and the production of Utah with that of California.

b The production of Alabama, Georgia and West Virginia is combined with Virginia, Arkansas is combined with Missouri, Texas with Kansas, and Utah and South Dakata with Colorado.

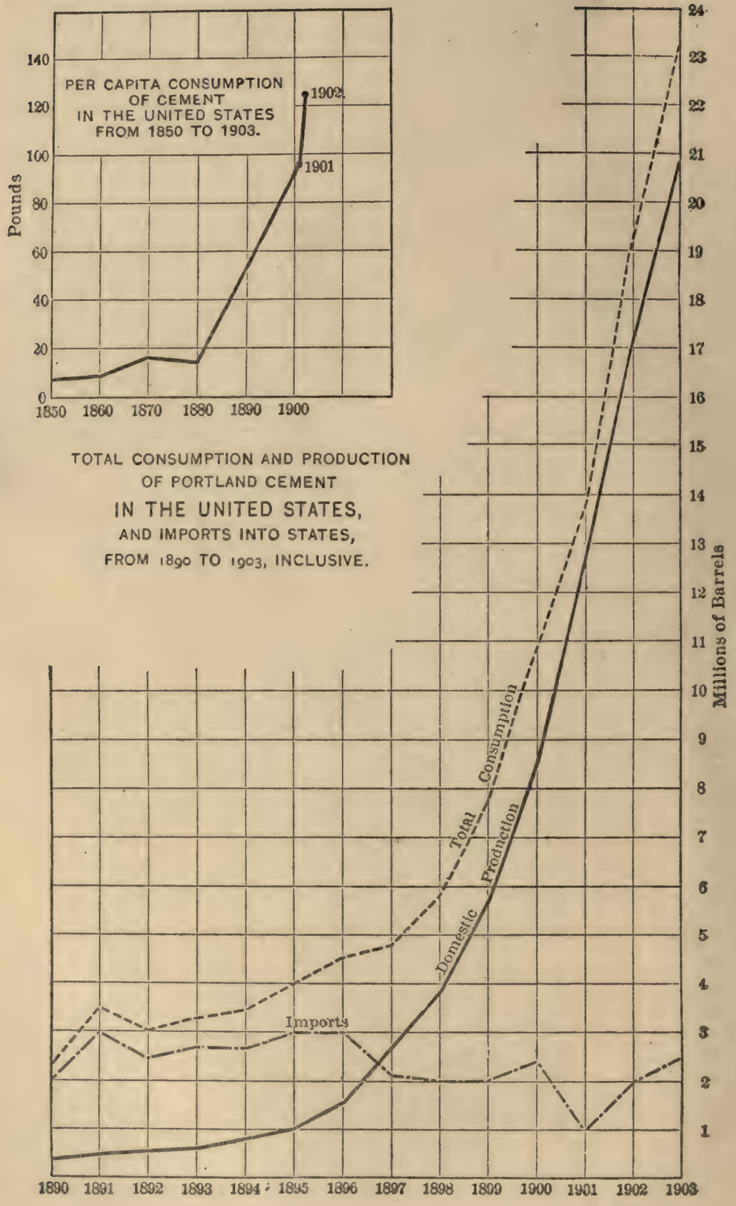
c The production of Alabama, Georgia and West Virginia is reported with Virginia, Missouri with Kansas, and Utah and Texas with Colorado.

TABLE V.—DEVELOPMENT OF THE PORTLAND CEMENT INDUSTRY IN THE UNITED STATES SINCE 1890.

(Mineral Resources United States, 1904.)

Section.	1890.			1900.			1902.		
	Number of works.	Quantity.	Per cent.	Number of works.	Quantity.	Per cent.	Number of works.	Quantity.	Per cent.
		Barrels.			*Barrels.*			*Barrels.*	
New York	4	65,000	19.4	8	465,832	5.5	10	1,156,807	6.8
Lehigh and Northampton Counties, Pa., and Warren County, N. J.	5	201,000	60.0	15	6,153,629	72.6	17	10,829,922	62.8
Ohio	2	22,000	6.5	6	534,215	6.3	7	563,113	3.3
Michigan	......	......	......	6	664,750	7.8	10	1,577,006	9.1
All other sections	5	47,500	14.1	15	663,594	7.8	21	3,103,796	18.0
Total	16	335,500	100.0	50	8,482,020	100.0	65	17,230,644	100.0

Section.	1. 03.			1804.		
	Number of works.	Quantity.	Per cent.	Number of works.	Quantity.	Per cent.
		Barrels.			*Barrels*	
New York	12	1,602,946	7.2	12	1,362,514	5.1
Lehigh and Northampton Counties, Pa	13	9,631,541	43.1	15	11,411,620	43.1
New Jersey	3	2,693,381	12.1	3	2,799,419	10.6
Ohio	8	729,519	3.3	7	910,297	3.4
Michigan	13	1,955,183	8.7	16	2,247,166	8.5
All other sections	29	5,730,403	25.6	30	7,774,871	29.3
Total	78	22,342,973	100.0	83	26,505,927	100.0



PER CAPITA CONSUMPTION OF CEMENT IN THE UNITED STATES FROM 1850 TO 1903.

TOTAL CONSUMPTION AND PRODUCTION OF PORTLAND CEMENT IN THE UNITED STATES, AND IMPORTS INTO STATES, FROM 1890 TO 1903, INCLUSIVE.

CHAPTER II.

THE NATURE AND COMPOSITION OF PORTLAND CEMENT.

Portland cement may be defined as "the finely pulverized product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials and to which no addition greater than 3% has been made subsequent to calcination[1]."

When the fine powder is mixed with water chemical action takes place, and a hard mass is formed. The change undergone by the cement mortar in passing from the plastic to the solid state is termed "setting." This usually requires but a few hours at most. On completion of the set a gradual increase in cohesive strength is experienced by the mass for some time, and the cement is said to "harden." Cements usually require from six months to a year to gain their full strength. Cement differs from lime in that it hardens while wet and does not depend upon the carbon dioxide of the air for its hardening. It is very insoluble in water and is adapted to use in moist places or under water where lime mortar would be useless. On pages 16 and 17 are two tables showing the analysis of various Portland cements.

Composition of Cement.

Portland cement, according to Le Chatelier,[2] consists of a mixture of tricalcium silicate, $3CaO.SiO_2$, and tricalcium aluminate, $3CaO.Al_2O_3$. He arrived at this conclusion after a long series of experiments, which consisted in examining thin sections of cement clinker under the polarizing microscope. He also made experiments upon the synthetic production of calcium silicates and aluminates by heating intimate mixtures of finely pulverized silica, alumina, and lime. He then examined into the hydraulic properties of the compounds so prepared. He, however, failed to prepare the tricalcium silicate directly by heating lime and silica, the

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[1] Standard Specifications, Amer. Soc. Test. Mat.

[2] Constitution of Hydraulic Mortars, (Trans. by Mack), and Annales des Mines, 1887, p. 345.

TABLE VII.—ANALYSIS OF AMERICAN PORTLAND CEMENTS.

(Made by the Author.)

	Where Made.	Made From.	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	SO_3	Loss.
1	New Jersey	Cement Rock and Limestone	21.82	2.51	8.03	62.19	2.71	1.02	1.05
2	“ “		21.72	2.50	6.62	61.89	3.71	1.22	2.04
3	Pennsylvania		22.20	2.27	6.69	62.61	3.00	1.32	1.56
4	“		21.94	2.37	6.87	60.25	2.78	1.38	3.55
5	“		20.32	2.58	7.30	63.93	2.57	1.27	0.83
6	Michigan	Clay and Marl	22.71	3.54	6.71	62.18	1.12	1.21	1.58
7	“		21.12	3.59	7.55	63.35	0.81	1.59	1.42
8	Ohio		21.41	2.15	6.88	62.72	1.44	1.57	2.18
9	“		21.86	2.45	5.91	63.09	1.16	1.59	2.98
10	Michigan	Clay and Alkali Waste	22.10	2.35	7.95	61.81	2.15	1.71	1.34
11	Virginia	Limestone and Clay	21.31	2.81	6.54	63.01	2.71	1.42	2.01
12	Missouri		23.12	2.49	6.18	63.47	0.88	1.34	1.81
13	Illinois	Blast Furnace Slag and Limestone	22.41	2.51	8.12	62.01	1.68	1.40	1.02

TABLE VIII.—ANALYSIS OF FOREIGN PORTLAND CEMENTS.

(Compiled from Various Sources).

Brand.	Where Made.	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	SO_3.
Alsen	Germany	20.48	3.88	7.28	64.03	1.76	2.46
Dyckerhoff	"	20.64	3.69	7.15	63.06	2.33	1.39
Germania	"	22.08	3.36	6.84	63.72	1.32	1.82
Hemmoor	"	21.14	4.01	5.95	63.24	1.44	1.47
Lagerdorfer	"	23.55	2.40	7.47	61.99	1.42	1.07
Condor	Belgium	23.87	2.27	6.91	64.49	1.04	0.88
Josson	"	22.92	2.46	7.98	63.39	Trace.	1.28
Caudlot	France	22.30	3.50	8.50	62.80	0.45	0.70
Boulogne	"	22.30	2.50	7.00	64.62	1.04	0.75
K. B. & S. Co.	England	19.75	5.01	7.48	61.39	1.28	0.96
White Bros.	"	22.74	3.70	7.74	57.38	0.57	0.97

result of the attempt being a mixture of lower silicates and lime, but gave it as his opinion that this compound could be prepared indirectly by heating together a mixture of fusible silicates and lime.

The tricalcium silicate is the essential element of Portland cement, in which it occurs in cubical crystals. In this compound the lime and silica bear the ratio of 168:60.4 or 2.78:1. From an analysis of Tiel "Grappiers" made by Hauenschild[1], it will be seen that they are approximately pure tricalcium silicate.

ANALYSIS OF TIEL "GRAPPIERS."

	Per cent.
Silica	23.6
Lime	64.7
Alumina	1.4
Ferric oxide	0.8
Magnesia	1.4
Sulphuric anhydride	0.5
Water	7.6
	100.0
Ratio of lime to silica	2.74 : 1

Theory of the Hardening of Cement.

Le Chatelier also examined thin sections of hardened cement under the microscope and found that it consisted of hexagonal plates of crystallized calcium hydroxide, $Ca(OH)_2$, embedded in a white matrix of interlaced needle-shaped crystals of hydrated monocalcium silicate, $(CaSiO_3)_2.5H_2O$. From these researches he concluded that the tricalcium silicate when mixed with water reacts to form a hydrated monocalcium silicate and calcium hydroxide according to the reaction,

$$2Ca_3SiO_5 + 9H_2O = (CaSiO_3)_2.5H_2O + 4Ca(OH)_2.$$

The calcium hydroxide then probably reacts further upon the calcium aluminate of the cement, forming hydrated basic calcium aluminate, $Ca_4Al_2O_7.12H_2O$.

$$Ca_3Al_2O_6 + Ca(OH)_2 + 11H_2O = Ca_4Al_2O_7.12H_2O$$

The "hardening" of cements is due to the first reaction, but the

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[1] Thonindustrie Zeitung, 1883, p. 418.

formation of the hydrated basic calcium aluminate probably exerts a marked influence upon the "setting" properties of the cement.

Hydraulic Index.

Assuming that three molecules of lime are united to one of silica to form the tricalcium silicate, that three molecules of lime are united to one of alumina to form the tricalcium aluminate, and that these two compounds are the essential ingredients of cement, Le Chatelier gives the following as the ratio between the lime and magnesia, the basic elements, and the silica and alumina, the acid elements in a good cement

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} \leqq 3 \qquad (1)$$

and

$$\frac{CaO + MgO}{SiO_2 - Al_2O_3 - Fe_2O_3} \geqq 3 \qquad (2)$$

Le Chatelier also states that (1) usually gives for a good cement from 2.5 to 2.7, and (2) from 3.5 to 4.

This ratio betwen the silica and alumina on the one hand and the lime on the other is termed *"hydraulic index."*

Erdmenger[1] has pointed out, however, that the above equations are not borne out by experience, as the assumption that lime and magnesia are of equal hydraulic value is an error.

Messrs. Newberry's Theories.

Messrs. Spencer B. and W. B. Newberry[1], in a series of researches as to the constitution of cement, arrived at conclusions quite different from those of Le Chatelier. They prepared silicates and aluminates of lime synthetically by heating together in a Fletcher gas furnace intimate mixtures of finely pulverized quartz and calcium carbonate, and alumina and calcium carbonate in different molecular proportions. They then examined into the hardening and setting properties of the resulting compounds. While these chemists agreed with Le Chatelier that the silica in cement is present as tricalcium silicate, and that to this is due the ultimate hardening of cement, they found no difficulty in prepar-

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[1] J. Soc. Chem. Ind., **11**, 1035.

ing the tricalcium silicate directly, by heating together silica and lime in the molecular proportion of 1 to 3. The Messrs. Newberry, however, from their experiments upon the calcium aluminates concluded that the alumina is in combination with the lime as dicalcium aluminate and not as tricalcium aluminate. Their experiments led them to the following conclusions:

"*First.*—Lime may be combined with silica in the proportion of 3 molecules to 1, and still give a product of practically constant volume and good hardening properties, though hardening very slowly. With 3½ molecules of lime to 1 of silica the product is not sound, and cracks in water.

"*Second.*—Lime may be combined with alumina in the proportion of 2 molecules to 1, giving a product which sets quickly, but shows constant volume and good hardening properties. With 2½ molecules of lime to 1 of alumina the product is not sound."

Newberry's Formula.

The formula for the tricalcium silicate, $3CaO.SiO_2$, corresponds to 2.8 parts by weight of lime to 1 part of silica, and the formula for the dicalcium aluminate, $2CaO.Al_2O_3$, corresponds to 1.1 parts of lime to 1 of alumina. From this the following formula is given as representing the maximum of lime which should be present in a correctly balanced Portland cement; per cent lime = per cent silica × 2.8 + per cent alumina × 1.1.

They found that cement prepared synthetically with lime, alumina, and silica proportioned according to the above formula gave good results, whereas that prepared by Le Chatelier's formula was unsound, showing the lime to be in excess.

Törnebohm's Investigations.

Törnebohm,[1] a Sweedish investigator, checked the microscopic work of Le Chatelier and identified in Portland cement four distinct mineral constituents which he called *Alit, Belit, Felit* and *Celit,* and described as follows[2]:—

"Alit is the preponderating element and consists of colorless crystals of rather strong refractive power, but of weak double refraction. By this he means that Alit in polarized light between

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[1] Kongreb des intern verb. für material prüff Stokholm, 1897.

[2] Richardson, Papers Asso. Port. Cem. Mfgs., June 15, 1904.

crossed Nicol prisms has insufficient optical activity to produce more than weak interference colors of a bluish gray order.

"Celit is recognized by its deep color, brownish orange. It fills the interstices between the other constituents and eventually forms the magma or liquid of lowest freezing point out of which the Alit is separated. It is strongly double refractive, that is to say, gives brilliant colors when examined between crossed Nicol prisms.

"Belit is recognized by its dirty green and somewhat muddy color and by its brilliant interference colors. It is bi-axial and of high index of refraction. It forms small round grains of no recognized crystalline character.

"Felit is colorless. Its index of refraction is nearly the same as that of Belit and it is strongly double refractive. It occurs in the form of round grains, often in elongated form, but without crystalline outline. Felit may be entirely wanting.

"Besides these minerals an amorphous isotropic mass was detected by Törnebohm and Le Chatelier. It is called isotropic because it has no effect upon polarized light. It has a very high refractive index.

"Törnebohm adds the important fact that a cement 4% richer in lime than usual consists almost entirely of Alit and Celit."

Richardson's Work.

Clifford Richardson, an American chemist, in a paper, read before the Association of Portland Cement Manufacturers at Atlantic City, N. J., June 15, 1905, described the results of a thorough and exhaustive microscopic study of Portland cement clinker. As the result of this investigation he again advanced the theory first brought forward by Winkler[1] in 1858, I believe, that Portland cement clinker is a solid solution. This paper is by far the most valuable argument, so far advanced, explaining the properties of cement along the lines of physical chemistry, and the investigations which led up to it, the most thorough so far undertaken. Richardson prepared many synthetic silicates and aluminates and determined their optical properties, hydraulic value and phyiscal characteristics. These he describes as follows:—

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[1] *Dingler's polyt. Jour.*, CLXXV, p. 208.

"Mono-calcic silicate- SiO_2CaO: A crystalline substance of high optical activity and little or no hydraulic properties. Specific gravity 2.9.

"Di-calcic silicate- SiO_2CaO, or more probably $2SiO_24CaO$: A definite crystalline compound of high optical activity and of very little hydraulic activity except in the presence of carbonic acid, but setting slowly in water, generally lacking volume constancy. Specific gravity 3.29.

"Tri-calcic silicate- SiO_23CaO, or more probably $2SiO_26CaO$: A definite crystalline silicate of low optical activity and corresponding in this respect with Alit. Its hydraulic activity is not great but greater than that of di-calcic silicate. If fused and reground it sets slowly like Portland cement. Specific gravity 3.03.

"Three definite silicates of calcium, therefore, exist, the two more basic ones being strongly differentiated from each other by their optical activity.

"Mono-calcic aluminate- Al_2O_3CaO: This aluminate is a crystalline substance of high optical activity, but it is not sufficiently basic to be found in a material of such basic character as Portland cement clinker. Specific gravity 2.90.

"Tri-calcic di-aluminate- $2Al_2O_33CaO$: This aluminate is one of highly crystalline character and of great optical activity, making it readily recognizable. Specific gravity 2.92.

"Di-calcic aluminate- Al_2O_32CaO: A substance crystallizing from a state of fusion in dendritic forms having no optical activity and being, therefore, isotropic. This differentiates this aluminate very sharply from the preceding one and makes the identification of the two materials very easy. Specific gravity 2.79.

"Tri-calcic aluminate- Al_2O_33CaO: This aluminate crystallizes from the fused condition in elongated octa-hedra. It is isotropic and it might at first be assumed that it was not a definite compound, but merely the di-calcic silicate crystallizing out of a magma of indefinite composition. It has been shown, however, by further investigations too lengthy to go into at this point to be undoubtedly a definite aluminate. Specific gravity 2.91."

Solid Solution Theory.

Richardson following the supposition that clinker is a solid solution, prepared clinkers of pure silica, alumina and lime, in the proportions met with in the industrial product. The proper molecular proportions were obtained by calculation from two very exact analyses of industrial clinker, just as is done in calculating the formula of a mineral, and the ratio 6 to 1 was chosen as representative of practical manufacturing conditions. Clinkers having the following formulæ were then prepared:—

$12(SiO_2\ 3CaO) + 2(Al_2O_3\ CaO) = 38\ CaO$
" " $+ 1(2Al_2O_3\ 3CaO) = 39\ CaO$
" " $+ 2(Al_2O_3\ 2CaO) = 40\ CaO$
" " $+ 2(Al_2O_3\ 3CaO) = 42\ CaO$

"Thin sections of these clinkers showed that the one corresponding to the substance present as mono-calcic aluminate contained a very considerable amount of Celit, that corresponding to the next higher degree of basicity, $2Al_2O_3 3CaO$, contained less, that corresponding to $Al_2O_3 2CaO$ still less, while that in which tri-calcic aluminate, $Al_2O_3 3CaO$, is supposed to be the form in which the aluminate is present contains no Celit, but is a pure Alit corresponding in every way with that seen in industrial Portland cement clinker.

"The composition of Alit is, in this way, entirely satisfactorily explained. It is a solid solution of tri-calcic silicate in tri-calcic aluminate. And on reflection it is readily seen that the di-calcic aluminate could not become dissolved in tri-calcic silicate without reaction going on and an interchange of base between the tri-calcic silicate and di-calcic aluminate to such an extent as to convert a portion of the di-calcic aluminate to the tri-calcic form and a corresponding portion of the tri-calcic silicate to the di-calcic form. The tri-calcic aluminate then dissolves in the tri-calcic silicate and the di-calcic aluminate in the di-calcic silicate, thus forming two separate and distinct solid solutions, the one Alit and other Celit, which, while no doubt miscible in the molten condition, are not so in the solid form. In the same way the interchange of bases in the clinkers of less basic form where the amount of lime was only sufficient to account for the presence of mono-calcic or tri-calcic di-aluminate, would result in a similar state of affairs, but with a much larger percentage of Celit as the basicity decreases."

Richardson also concludes[1] that the setting of Portland cement is almost entirely due to the decomposition of the Alit, examination showing the Celit to be almost unattacked; and that the strength of Portland cement after setting is due entirely to the crystallization of calcium hydrate under certain favorable conditions, and not at all to the hydration of the silicates and aluminates. His theory is that "on addition of water to the stable system made up of the solid solutions which compose Portland cement, a new component is introduced, which immediately results in lack of equilibrium, which is only brought about again by the liberation of free lime. This free lime the moment that it is liberated, is in solution in the water, but owing to the rapidity with which it is liberated from the aluminate, the water soon becomes supersaturated with calcic hydrate and the latter crystallizes out in a network of crystals, which binds the particles of undecomposed Portland cement together." The initial set is due to the aluminates, while subsequent hardening is due to the slower liberation of lime from the silicates.

Substances Found in Cement.

All these investigators agree that the essential ingredients of Portland cement are lime, silica, and alumina. A little of the alumina is always replaced by ferric oxide and some of the lime by magnesia. Small percentages of alkalies, potash and soda, present in the clay as silicates, are also in cement, while the most thorough burning fails to drive off all the carbon dioxide from the limestone or marl in the raw mixture, leaving a trace in the finished product. This trace is increased by the absorption of this constituent from the atmosphere. Water is also absorbed from the air and traces of manganese, titanium, phosphorus, strontium, ferrous oxide and sulphides are usually present in Portland cement. In analyzing cement it is generally sufficient to know the silica, lime, alumina and ferric oxide together, and the magnesia; less

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[1] Papers Association of Portland Cement Manufacturers, Dec. 14, 1904.

often the alumina and ferric oxide separately, the sulphuric acid and the carbon dioxide, while more rarely yet the alkalies, combined water, and the sulphur present as sulphate and sulphide respectively.

Lime.

A good cement contains from 58 to 67 per cent lime, the amount depending upon the relative proportions of silica and alumina, and also upon the care with which the cement has been manufactured. Up to the limit, it may be said, that the more lime that is present in a cement the greater will be its strength. The limit is reached, however, when more lime is present than will combine chemically with the silica and alumina, leaving some lime in the uncombined state. Lime in slaking expands so that an excess of lime over what will unite with the silica and alumina will cause the cement to expand, or "blow" as it is technically termed, and crack.

High lime cements are usually very slow setting, but harden rapidly, sometimes reaching their maximum strength in 28 days. After this time, retrogression apparently takes place in the strength of neat test pieces subjected to tension and much discussion has taken place as to whether this is due to internal disruption of the briquettes or merely to the fact that the increasing hardness has made them brittle, and consequently likely to be fractured by the distortion met with in breaking such a short piece rather than to the tensile stress applied. This latter theory seems to be the true one, as compression specimens seldom show such retrogression at longer periods. The sand briquettes also usually show some increase of strength with time, even when the neat ones fail. Provided a cement is sound, there is nothing in the theory that cements which harden slowly and show progressive gain are any better than those which harden promptly, and a cement which reaches its maximum strength promptly would seem to anyone who gives the matter consideration much more desirable than one which takes several years to reach the same point.

Cements low in lime usually contain clay in excess, for sufficient lime was not originally present in the raw material to change all the clay to silicates and aluminates. This excess of clay, of course, is devoid of cementing qualities and may be looked upon as just so much foreign matter. Though it will not cause the cement to fall to pieces subsequently, it takes away from its strength because in its place should be cement. Low lime cements are apt to be "quick setting." Hence, one of the remedies for "quick setting" cement is to increase the lime content of the raw mixture. For this reason high alumina cements often contain more lime than those low in alumina, in spite of the fact that alumina combines with less lime than does silica.

The amount of lime a cement will bear depends upon the care with which the mixture of raw materials is made. Thus poorly ground, imperfectly mixed raw materials would probably result in a very much over-limed cement, if the lime limit (as shown by chemical analysis of the clay, marl, limestone or cement rock of the mixture) was anywhere near reached; for the coarse particles of calcium carbonate would not come into sufficiently close contact with the silica and alumina to completely combine with the latter. A properly burned cement will also stand a greater percentage of lime than an improperly burned one. A cement in which the temperature at burning was too low to heat all the lime to the point of combination with the silica and alumina, would naturally contain free lime. Chemical analysis, therefore, if taken alone as the guide to a cement, will seldom tell us much where the lime content is concerned; as of two cements containing the same quantity of lime, one properly made might be quite sound while the other, from faulty mixing and burning, might be anything but sound.

Most of the Portland cements made in the United States, in the rotary kiln, contain when freshly ground between 61 and 64 per cent lime, with about 63 per cent for an average. Cement after standing of course contains much less lime than this because the absorption of water and carbon dioxide lowers the percentage of lime. The percentage of lime to be carried at any works is usually controlled by two things, the "setting time" and the "soundness." There must be enough lime present to keep the cement from being quick setting, either when made or after seasoning, and there must not be so much lime present that the cement will fail on the soundness test. With raw materials high in alumina, the margin between the maximum and minimum limits is small. With such materials extreme care is needed in the process of manufacture and the raw materials should be very finely ground, and the burning thorough. When the alumina is low the margin is much greater, but, if the lime is carried near the maximum, a stronger cement will result.

Silica.

Silica is, of course, next to lime the most important constituent of Portland cement and present in the next largest proportion. Portland cements usually contain from 19 to 25 per cent silica. Those containing the latter figure are usually low in alumina and those containing the former are high in alumina. High silica cements are usually slow setting and of good tensile strength. Increasing the silica usually increases both the strength and setting time. It increases the temperture of burning, also, however. Cement should contain at least 2.5 times as much silica as alumina in order to prevent its being quick setting. Since the silicates available for cement manufacture usually contain too much alumina for this proportion, clays, containing some free or uncombined silica are the source of the silica in cement. In increasing the silica in the unburned cement mixture, therefore, clays having this free silica in such a fine state of subdivision, that it may easily combine with the lime, must be selected and not clays in which the free silica is present as quartz, pebbles, etc. For the same reason the silica in cement can never be increased by the addition of quartz or flint to the raw materials, but instead another and more silicious clay, shale or cement rock must be found and used in place of, or mixed with the high alumina, clay, etc.

Alumina.

Portland cement usually contains between 5 and 10 per cent alumina. As the percentage of alumina rises, the cement becomes more quick-setting. When the percentage of alumina rises above 10 per cent the cement becomes very quick-setting, with a corresponding decrease of tensile strength. This is to be expected, since the strength of cement is due to the calcium silicate, and its setting properties to the calcium aluminate. As the calcium aluminate is very fusible, the clinkers obtained on burning mixtures high in alumina are very fusible, hard to burn uniformly and difficult to grind. Cement clinkers made from kaolin show all of these properties and the finished cement is low in tensile strength.

Ferric Oxide.

According to Le Chatelier, ferric oxide and calcium carbonate on burning yield products which slake with water and possess no hydraulic properties. Schott, however, prepared cement containing only lime, silica and ferric oxide, which showed excellent hardening qualities, and therefore concluded that alumina could be completely replaced by ferric oxide without diminishing in any way the hydraulic properties of cement. S. B. and W. B. Newberry from their researches concluded that ferric oxide and alumina act in a similar manner in promoting the combination of silica and lime.

Zulkowsky also made experiments along this line and his conclusions agree with those of Schott and Newberry, and it is now generally agreed that the iron oxide in the cement mixture acts as a flux and promotes the combination of the silica and the lime. Mixtures of silica, alumina, and lime, in the proportions usually found in cement, are extremely hard to burn. The replacement of part of the alumina by iron, however, greatly lowers the temperature of burning. One of the cures for unsound cement is therefore found in the replacement of clays high in alumina by those high in iron. As iron does not seem to make cement quick-setting, iron may be made to replace alumina to advantage in many instances. In mixtures high in silica and consequently hard to burn, the addition of some soft iron ore, such as brown hematite, to the mix should lower the temperature at which clinkering takes place and make it easier to produce a sound cement.

Of late years numerous authorities have come forward advocating Portland cement containing high percentages of ferric oxide for use in sea water, claiming for such cements great resistance to the disintegrating influence of the salts of magnesium, etc., found in sea water. This claim seems well backed by experiments and theory and deserves a thorough investigation.

The amount of ferric oxide in cements is usually small, less than 5 per cent. The dark gray color of cement is due to the presence of iron compounds. Cement prepared from silica, lime, and alumina only is colorless, but upon replacing the alumina by ferric oxide the cement becomes gray.

Magnesia.

A cement containing 1½ per cent of magnesia was long considered dangerous; now 4 per cent in cement is thought to be harmless, and many authorities allow even 5 per cent magnesia. The popular supposition is that magnesia in considerable percentages causes cement in time to expand and crack. R. Dykerhoff presented to the German Association of Cement Manufacturers in 1895 the results of a very thorough research into the effects of magnesia. From his experiments he concluded that magnesia, whether added to a normal mixture or substituted for an equivalent portion of lime, causes a decrease of strength in the resulting cement, when present in more than 4 per cent. Cracking only occurred with 8 per cent or more magnesia. A commission from the American Association is now studying the effects of magnesia. Le Chatelier in his formula considers magnesia to replace lime, while the Newberrys in their formula consider it inactive and not to replace lime.

Authorities differ as to the hydraulic values of magnesium silicates. Fuch, Lieven, Rivot, Kawalewsky, and Zulkowski all prepared magnesium cements, while S. B. and W. B. Newberry and Held were not able to prepare compounds of any hydraulic value from magnesia. It is probable, however, that if these magnesian silicates have any real hydraulic value they are at least inferior to the lime silicates and hence magnesia may be considered a disadvantage in cement, in that it takes the place of a more active and important lime compound. Whether magnesia should be considered in calculating cement mixtures is also a debated point, and one with which the hydraulic value of the magnesian compounds has nothing to do, as the question is simply whether or not the magnesia is combined with silica and alumina in cement. If it does combine, enough of the silica and alumina should be present, not only to form the proper lime compounds, but also the proper magnesian compound, or else the cement will be too basic and will probably contain an excess of uncombined lime.

The standard specifications place the maximum amount of magnesia (MgO) allowable in a Portland cement at 4 per cent.

Alkalies.

Potash and soda are present in all cements in small quantities, usually less than 0.75. A large proportion of the alkalies present in the raw material are driven off in burning. Experiments made by the writer with the cement rock of the Lehigh Valley indicate that at least one-half the potash is lost in the kiln, passing off in the kiln gases. The loss of soda is, of course, much less since this is the less volatile of the two alkalies. It is supposed that the alkalies act as a flux and promote the combination of the silica and the alumina with the lime, and experiments made by the writer with small kilns certainly confirm this theory.

The addition of small quantities of either the carbonates or the hydroxides of potash and soda will cause cement to set quickly, and it is probable that the presence of any considerable quantity of alkali in cement would cause it to set quickly. When quick setting cement is due to the presence of the alkalies, the trouble can be remedied, to some extent, by raising the temperature of burning, thus volatilizing the alkali. Cements made from alkali waste often contain large quantities of potash and soda, in some cases the amount reaching as high as 2.5 per cent. Butler[1] states that instances have occurred in which these cements gave anything but satisfactory results, and the only fault that could be found with their chemical composition was a slight excess of alkali. In most cement the alkalies are present in such small quantities that their effects are of little hydraulic importance.

Sulphur.

Several compounds of sulphur are present in cement; chief of these are calcium sulphate and calcium sulphide. The action of calcium sulphate upon cement is to delay the set. For this reason it is always added in the form of gypsum or plaster of Paris to the cement after burning. The standard specifications so far recognize the necessity for the addition as to allow manufacturers to

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[1] Portland Cements, by R. D. Butler, p. 263.

employ a proportion not exceeding 3 per cent. in order to confer to the cement, slow-setting properties. Although the presence of calcium sulphate in small quantities is beneficial to cement, there is no doubt that a quantity exceeding 4 or 5 per cent. is injurious.

The standard specifications allow 1.75% sulphur trioxide (SO_3) in Portland cement. The retrogression often met with in neat Portland cement briquettes is often attributed to the presence of calcium sulphate in the cement. My own experiments, however, made with cements to which no gypsum had been added, and the same cement with the addition of 2 per cent. gypsum, do not indicate this, as, in most cases, where retrogression occurred in the cement to which sulphate had been added, it also occurred with the unsulphated cement. Sulphates increase the strength of cement, and if they are present in larger amounts than 2 or 3 per cent., will unquestionably cause higher short time tests than the long period ones, though this may be due merely to the test pieces becoming brittle. The presence of sulphates in cement promotes soundness, or at least enables some cements to pass the accelerated tests. The property of gypsum and plaster of Paris to retard the set of cement is touched upon to greater length in the section on "Setting Time."

Carbon Dioxide and Water.

Carbon dioxide and water are present in all cements, the amount usually varying with the age of the cement. Freshly-ground cements usually show less than 1 per cent. of these two constituents combined, while well-seasoned ones may show as much as 3 or 4 per cent. Underburned cements may, or may not, show high loss on ignition. It is possible to drive off all the carbon dioxide from the raw material, and yet not bring the mass to the point of incipient vitrifaction necessary to produce a sound clinker. Samples of underburned clinker will frequently show a loss on ignition (water and carbon dioxide) as low as that of well-burned cement. If the sample is left in the air, however, it soon shows a very high loss on ignition, due to absorption of water and carbon dioxide from the air. Some of the water present in cement can be driven off at 110° C, while some of it requires a red heat for its expulsion. Determinations of loss on ignition, unless very high, are, as a rule, of little help in determining the quality of cement, since an amount as high as 4 per cent. may be due to "aging" of the cement, which is recognized as beneficial to it. The standard specifications wisely make no requirements as to the maximum limit for loss on ignition.

Other Compounds in Portland Cement.

Besides the compounds mentioned above, cement usually contains small amounts of Titanic Acid, Ti_2O_3; Ferrous Oxide, FeO; Manganous Oxide, MnO; Phosphorus Pentoxide, P_2O_5; and Strontium Oxide, SrO. It is doubtful if these compounds have any effect on the hydraulic or setting properties of Portland cement when present in the minute quantities usually found in commercial cements. It is probable that titanic acid can be substituted for silica, but this cement would be hard to burn; Manganese Oxide acts as a flux and cements have been made in which Strontium replaced lime.

The author found in three Portland cements from the Lehigh District the amounts of the rarer constituents stated below:

	Cement No.		
	1	2	3
Titanic Acid	0.28	0.27	0.32
Ferrous Oxide	0.23	0.16	0.11
Manganous Oxide	0.06	0.08	0.09
Strontium Oxide	0.08	...	....
Calcium Sulphide	0.18	0.09	0.07
Potash	0.50	0.48	0.59
Soda	0.26	0.31	0.38
Phosphorus Pentoxide	0.25	0.31	0.29

MANUFACTURE.

CHAPTER III.

RAW MATERIALS.

Essential Elements.

As we have seen from the preceding chapter the essential elements of Portland cement are silica, SiO_2, alumina, Al_2O_3, and lime, CaO. Silica and alumina both exist pure in nature, the first as quartz and flint and the second as corundum or emery. Neither quartz nor corundum are suitable for cement making, because of their extreme hardness and the impossibility of reducing them to the degree of fineness necessary for their combining with the lime. Silica and alumina, however, together are the essentials of clay (or shale) and this is the source of these elements for cement manufacture. Lime is not found free in nature, but combined with carbon dioxide forms calcium carbonate, $CaCO_3$, which occurs in many parts of the country under the names limestone, chalk and marl. Most limestones contain some clay and when this is present to the extent of 18 or more per cent. what is known as "cement rock" or argillaceous limestone results. Certain by-products of other industries contain one or more of the essential elements of Portland cement in a condition, and in proportions suitable for Portland cement manufacture. In this country, blast furnace slag is now used and caustic-soda waste has been tried.

Classification of Materials.

Portland cement may be and is manufactured from a variety of raw materials. Those used may be classed under two general head, (1) calcareous, (2) argillaceous, according as the lime or the silica and alumina predominate.

Calcareous.	*Argillaceous.*
Limestone,	Clay,
Marl,	Shale,
Chalk,	Slate,
Alkali waste,	Blast-furnace slag.
	Cement rock.[1]

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[1] Cement rock may be considered as either calcareous or argillaceous. Usually it may be classed as the latter, but in the neighborhood of Nazareth, Pa., the rock in several places runs so high in lime as to necessitate the use of slate or clay with it.

Any combination of materials from these two groups may be used which will give a mixture of the proper composition for burning (See Chapter IV), but so far the ones used in this country are:—

1. Cement-Rock and Limestone.—Used in the famous Lehigh Valley cement district in which more than half of the cement manufactured in this country is produced. This district comprises Berks, Lehigh and Northampton Counties in Pennsylvania, and Warren County, New Jersey. In 1903, 55.2 per cent. of the total output of the country was manufactured from this combination.

2. Marl and Clay or Shale.—Used principally in Michigan, Ohio, Indiana and Central New York.

3. Limestone and Shale or Clay.—Used in many parts of the country as these materials are widely distributed.

4. Blast Furnace Slag and Limestone.—Plants are now located for the manufacture of cement from these materials in Illinois, Ohio,, and Pennsylvania. These plants together had a rated capacity of about 700,000 barrels per year in 1904.

5. Caustic Soda Waste and Clay, formerly used by one large alkali plant in Michigan.

Limestone.

Limestone is abundantly distributed throughout the country and occurs in many geological periods. It consists essentially of carbonate of lime (or calcium carbonate, $CaCO_3$,) and when pure forms the mineral calcite. The principal foreign elements found in limestone are silica, iron oxide, alumina, carbonate of magnesia and the alkalies, potash and soda. Limestone sometimes contains considerable carbonate of magnesia and when this reaches 45 per cent. of the total carbonates, it is known as dolomite. To be suitable for cement manufacture limestone should contain but little carbonate of magnesia—5 per cent. being about the limit. It should also be free from quartz either in the form of sand or flint pebbles. Occasional veins of flint running through the limestone bed will not hurt, since this may be sorted out in quarrying.

Since the limestone must be reduced to a fine powder in order to intimately mix with the clay or shale used with it, its hardness is an important factor in determining its suitability for cement making. As an usual thing pure limestone is very much harder than the impure clayey ones, consequently the less pure limestones are really much better for cement manufacture than the hard, pure ones. The greatest factor in the making of a sound cement is the fine grinding of the raw materials. Indeed most plants using limestone and clay have found the grinding of the mixture to the degree of fineness necessary to give the cement a good hot test, when fresh, a very difficult proposition. Some of them have found it preferable on the score of economy not to make their fresh cement pass the soundness test, but to let it season sound in their bins.

Such cement provided it *has* seasoned sound is as good as any and there should be no prejudice against its use.

In South Dakota and in Alabama there are found certain rotten limestones or chalks, more or less impure in composition and easily ground. The former deposit has been used for some time and the latter has been lately utilized for Portland cement manufacture. The ease with which these chalks or rotten limestones can be ground is a decided point to their advantage, and makes them most valuable raw materials.

On the following page is a table giving the analyses of some limestones used for Portland cement manufacture:

Cement Rock.

The impure clayey limestone, used for the manufacture of Portland cement in the Lehigh District, is known technically as "cement rock." This rock forms a narrow belt extending in a northeasterly direction from Reading, Pa., to a few miles north of Stewartsville, N. J. It passes through the counties of Berks, Lehigh and Northampton, in Pennsylvania, and Warren County, New Jersey, and is about fifty miles long and not over four miles at its greatest width. There were in January, 1905, located in this district eighteen Portland cement companies in active operation, one other mill completed and nearly ready to begin operation and two in process of construction. The mills of this district produced in 1903 over 55 per cent. of the output of the country.

TABLE IX.—ANALYSES OF LIMESTONES USED IN MANUFACTURE OF PORTLAND CEMENT.

<table>
<tr><th>USED BY</th><th>Silica, SiO_2</th><th>Iron Oxide, Fe_2O_3</th><th>Alumina, Al_2O_3</th><th>Carbonate of Lime, $CaCO_3$.</th><th>Carbonate of Magnesia $MgCO_3$.</th><th>Used with</th></tr>
<tr><td>Alpena Port. Cem. Co., Alpena, Mich</td><td>0.42</td><td colspan="2">0.18</td><td>98.14</td><td>0.98</td><td>Clay</td></tr>
<tr><td>Catskill Cement Co., Smith's Landing, N. Y</td><td>1.54</td><td>1.04</td><td>0.39</td><td>96.16</td><td>1.09</td><td>Clay</td></tr>
<tr><td>Glens Falls Port. Cem. Co., Glens Falls, N. Y</td><td>3.30</td><td colspan="2">1.30</td><td>93.09</td><td>3.31</td><td>Clay</td></tr>
<tr><td>Marquette Cem. Mfg. Co., LaSalle, Ill</td><td>8.20</td><td colspan="2">1.30</td><td>88.16</td><td>1.78</td><td>Clay</td></tr>
<tr><td>Pacific Port. Cem. Co., Suisun, Cal</td><td>0.41</td><td colspan="2">0.56</td><td>97.92</td><td>0.44</td><td>Clay</td></tr>
<tr><td>St. Louis Port. Cem. Co., St. Louis, Mo</td><td>0.75</td><td colspan="2">0.35</td><td>98.15</td><td>0.20</td><td>Clay</td></tr>
<tr><td>Southern States Port. Cem. Co., Rockmart, Ga</td><td>0.52</td><td>1.00</td><td>0.26</td><td>94.68</td><td>4.24</td><td>Shale</td></tr>
<tr><td>Limestone from Nazareth, Pa</td><td>3.66</td><td colspan="2">2.10</td><td>92.13</td><td>2.21</td><td>Cement rock</td></tr>
<tr><td>Limestone from Coplay, Pa</td><td>2.14</td><td colspan="2">1.46</td><td>94.35</td><td>2.18</td><td>"</td></tr>
<tr><td>Limestone from Annville, Pa</td><td>0.36</td><td colspan="2">0.45</td><td>97.11</td><td>1.12</td><td>"</td></tr>
</table>

It has been found by experience that a mixture containing about 75 per cent. carbonate of lime and 18-20 per cent. of clayey matter (silica, iron oxide and alumina) gives the best Portland cement, and the impure limestones found in the Lehigh Valley approach more or less nearly this composition. When this cement rock contains less than 75 per cent. carbonate of lime it is the practice here to add sufficient purer limestone to make the mixture of this proportion. At several mills around Nazareth the rock contains more than 75 per cent. carbonate of lime and here instead of adding limestone it is necessary to add a little slate or clay to lower the percentage of lime.

Geologically this cement rock is Trenton limestone of the lower Silurian age, and lies between the Hudson shales and the Kittatinny magnesian limestone. The upper beds of the cement rock, where it comes in contact with the slate are more or less shaley in composition and slatey in appearance and fracture. Often here the rock contains less than 50 per cent. carbonate of lime and is not suited to the manufacture of Portland cement. As we go lower in the formation the lime increases until near the base of the formation, in contact with the Kittatinny limestone it may carry as high as 95 per cent. carbonate of lime. It is from these lower beds that the limestone necessary for mixing with the cement rock is obtained. The Kittatinny limestone itself is too high in magnesia (15 to 20 per cent. MgO) to use for cement making, but there are a few beds in this formation low enough in magnesia to use successfully. The cement rock itself often carries 5 to 6 per cent. magnesium carbonate but is never so high in this element as the Kittatinny limestone. The purest limestone in use in the district contains about 98 per cent. carbonate of lime and comes from Annville, Pa., some 50-70 miles away.

Cement rock is considerably softer than the pure limestones, usually used with clay, consequently it is much more easily ground. The nearer it approaches the correct composition for cement mixture the more valuable it is. In general, it may be said that rock requiring a small admixture of clay will prove more economical than one requiring addition of limestone for a proper mixture; since, in nearly every instance, the cement rock is overlaid by clay which has to be removed anyhow, while the limestone may have to be bought or at least quarried. Equally desirable is the combination of a high and a low lime cement rock.

The quantity of limestone added at some of the cement mills in the Lehigh District is as much as 50 per cent. of the rock itself, and it is no uncommon thing when limestone is bought to have this item alone cost from 5 to 10 cents per barrel of cement produced. A ton of cement rock and limestone mixture ready for the kilns will produce from 3.1 to 3.3 barrels of cement. The approximate quantity of limestone necessary to use with any cement rock whose analysis is known may be found as follows:—

If the lime is reported as carbonate, $CaCO_3$, Quantity Limestone Necessary

$$= \frac{75 - (\%\ CaCO_3 \text{ in Cement Rock})}{(\%\ CaCO_3 \text{ in Limestone}) - 75} \times 100$$

If the lime is reported as lime, CaO, Quantity Limestone Necessary

$$= \frac{42 - (\%\ CaO \text{ in Cement Rock})}{(\%\ CaO \text{ in Limestone}) - 42} \times 100$$

The result in either event will be the number of pounds of limestone it is necessary to add to 100 pounds of cement rock, to make a mixture of approximately correct composition for burning.

Below will be found a table giving the analysis of some cement rocks of the Lehigh District and also a very complete analysis made by the author of a sample of rock of practically exact composition for burning, used by the Dexter Portland Cement Co., Nazareth, Pa. This is followed by an equally complete analysis of a mixture of Annville Limestone and cement rock, used by the Vulcanite Portland Cement Co., Vulcanite, N. J., made by W. F. Hillebrand, of the U. S. Geological Survey. This mixture is over clayed, however, and undoubtedly is merely a chance sample and not representative of that company's usual practice.

As will be seen by a reference to table X, there is a considerable difference in the analysis of the various samples. Not only is this true between samples from different quarries of the district but also between samples from the same quarry. This is shown by table XII, each sample of which represents an average of 11 drill holes of 16 feet each.

TABLE X —ANALYSES OF CEMENT ROCK USED FOR MANUFACTURE OF PORTLAND CEMENT.

Locality.	Silica, SiO_2,	Iron Oxide, Fe_2O_3	Alumina, Al_2O_3	Carbonate of Lime, $CaCO_3$	Corbonate of Magnesia $MgCO_3$
Nazareth, Pa........	18.15	1.61	7.21	68.14	3.88
Nazareth, Pa........	11.10	1.24	4.42	77.60	4.17
Stockertown, Pa.....	18.94	1.56	5.42	68.53	3.91
Siegfried, Pa	17.32	2.04	7.07	68.91	4.28
Coplay, Pa..........	14.71	2.10	6.61	69 54	5.11
Alpha, N. J..........	15.05	1.27	9.02	70.10	3.96
Stewartsville, N. J...	16.16	1.25	6.98	70.38	3.90
Northampton, Pa....	19.06	1.14	4.44	69.24	4.21

TABLE XI.—COMPLETE ANALYSES OF CEMENT ROCK AND CEMENT ROCK-LIMESTONE MIXTURE.

	Cement Rock.	Mixture.
SiO_2	13.44	15.18
TiO_2	0.23	0.23
Al_2O_3	4.55	4.94
Fe_2O_3	0.56	0.95
Feo	0.88	0.46
FeS_2	....	0.38
MnO	0.06	0.05
CaO	41.84	40.31
MgO	1.94	1.65
Na_2O	0.31	0.15
K_2O	0.72	0.97
P_2O_5	0.22	0.21
S	0.33	....
C	0.75	0.54
CO_2	32.94	32.38
$H_2O + 105$	1.55	1.31
$H_2O - 105$	Dried Sample	0.38
	100.32	100.09

TABLE XII.—SHOWING THE VARIATIONS IN THE COMPOSITION OF CEMENT-ROCK FROM SAME QUARRY.

Bench.	Section of Bench.	Analyses.			
		SiO_2.	$Fe_2O_3+Al_2O_3$	CaO.	MgO.
First 16 feet.....	West A......	16.26	7.22	70.37	3.95
" " "	West B	14.56	8.64	72.33	3.53
" " "	Center C.....	16.38	7.90	69.59	3.77
Second 16 feet...	West A......	17.34	7.94	67.93	4.19
" " " ...	West B	18.94	6.98	68.53	3.91
" " " ...	Center C.....	15.54	7.10	71.04	4.12
" " " ...	East D.......	17.02	7.30	69.34	4.16
" " " ...	East E.......	21.36	9.00	65.41	3.96
Third 16 feet....	West A......	21.98	8.80	62.65	4.87
" " "	West B	27.00	8.10	69.12	4.73
" " "	Center C.....	16.86	8.14	68.54	5.07
" " "	East D.......	24.16	9.14	60.69	4.32
" " "	East E.......	21.15	9.51	59.09	4.64
Fourth 5 feet....	Center C.....	25.16	8.28	60.42	4.27

Marl.

Cement is now made from marl in Michigan, Ohio, New York, and Northern Indiana. Practically all the cement made in Michigan is made from marl and clay or clay-shale, the only exceptions, at this writing, being the Alpena Portland Cement Co., which uses limestone and shale found in the immediate neighborhood of the plant, and the Wyandotte Portland Cement Co., which manufactures cement from clay and limestone, which are shipped to the works from accessible points on the lakes. In the southern peninsular are located the plants of the Bronson Portland Cement Co., at Bronson; of the Peerless, at Union City; of the Wolverine, at Coldwater and at Quincy; of the Omega, at Mosherville; and of the Peninsular, at Cement City, near Jackson. These mills are all located around Coldwater and Jackson, Mich. Fifty miles further to the northeast, are the mills of the Egyptian Portland Cement Co., and of the Aetna, at Fenton. Still farther north on the shores of Saginaw Bay is located the Hecla Cement Co.'s plant. In the west of Michigan, on the Muskegon River, the water power, of which it uses for grinding, etc., is located the Newaygo Portland Cement Co., at Newaygo, and north of this, at Marlboro, is found the Great Northern Portland Cement Co. Further north in the lower penisular, the one on one side and the other on the other side of the State, are the plants of the Elk Portland Cement Co., at Elk Rapids, and of the Alpena, at Alpena. From this general outline of the location of the various plants in Michigan, in January, 1905, it will be seen that there is no cement belt here, the materials for making cement being widely scattered throughout the State and there being an abundance of clay and marl in many sections.

In Indiana Portland cement is manufactured from marl at Stroh, La Grange County, by the Wabash Portland Cement Co., and at Syracuse, Kosciusco County, by the Sandusky Portland Cement Co. Both of the mills are in the northern part of the State and are only a few miles apart. In Ohio marl and clay are used at Harper, Logan County, by the Buckeye Portland Cement Co.; at Castalia, by the Castalia Portland Cement Co.; and at Sandusky, by the Sandusky Portland Cement Co. All of these plants are located in the northern part of the State near the lake. In New York marl is used by the Empire Portland Cement Co., at Warners; the Thomas Millen Co., at Wayland; the Wayland Portland Cement Co., at Wayland; the American Cement Co., at Jordan; and the Iroquois Portland Cement Co., at Caledonia. The latter plant has a dry marl and consequently uses the dry process.

Marl is more or less pure carbonate of lime, the principal impurities being clay, organic matter and carbonate of magnesia. Marl beds usually occupy the bodies of ancient extinct lakes or else the bottoms and banks of present ones and are formed by the precipitation of calcium carbonate from the water by the agency of certain algæ or water plants. In many instances the process of making marl beds is still going on. Marl is soft and pulverulent, sometimes containing many small shells, but usually the larger part of it passing a 200-mesh cement testing sieve. It therefore requires little grinding before burning. White marls usually are free from organic matter, but the grey marls often contain from 5 to 10 per cent. of impurities. Marl beds vary in size from a few acres up to two or three hundred. Some of the companies in Michigan each have marl beds aggregating over 1000 acres and measuring an average of 20 feet deep. Prof. Campbell has found that a cubic foot of marl contains 47.5 pounds of marl and generally about 48 pounds of water. As excavated and sent to the mill, however, it frequently contains much more water than the above figure.

Marls for use in Portland cement manufacture should be free from sand and pebbles. It is, of course, possible to separate the former from it by wash mills and the latter by specially designed screens. Either operation adds to the cost of manufacture, however. Some marls contain a considerable percentage of sulphur. From experiments made by the author, he is inclined to think that most of this sulphur is lost in the kiln. If present in the form of iron pyrites or in combination with organic matter, it is simply burned away. If present as calcium sulphate it is liberated by the combination of the lime with the silica. Exactly how much sulphur is allowable the author is not prepared to say, but it seems probable that at least 5 or 6 per cent. SO_3 might be present without rendering the marl unfit for the manufacture of Portland cement. Johnson[1] succeeded in making a sound true Portland cement, containing only 1.83 per cent. sulphur, in a small experimental kiln from a mixture of clay and gypsum. The raw material used by the Colorado Portland Cement Co., at Portland, Col., contains considerable gypsum, often as high as 7 or 8 per cent., yet the resulting cement contains only a normal amount of sulphate.

Some marls are sticky and pasty in texture and ball together as clay does. Such marls are hard to move from one part of the mill to another and require the addition of more water, which has subsequently to be evaporated in the kilns, in order to pump them about.

The value of a marl bed will usually lie in its depth and

[1] Cement and Engineering News, January, 1905, p. 11.

area and physical characteristics rather than its chemical composition. Marl must, of course, contain at least 75 per cent. of carbonate of lime after drying and deducting the organic matter and it should not contain over 2 or 3 per cent. free silica (silica as quartz sand) nor more than 5 per cent. carbonate of magnesia. The greater the depth of the bed the more economically it can be worked. If the beds are dry so that the dry process of manufacture can be employed the value of the deposit is greatly increased thereby.

Usually marls require the addition of about one-fifth their weight (when dry) of dry clay for burning. The approximate proportion in a specific case may be found as follows:

$$\text{Weight of Clay} = \frac{(\%\ \text{CaO in Marl}) - 42}{42 - (\%\ \text{CaO in Clay})} \times 100$$

The result gives the weight of clay (in pounds) to be added to 100 lbs. of marl. If in the analysis lime is reported as carbonate of lime, multiply this percentage by 0.56 for the equivalent percentage of lime, CaO.

Table XIII gives the analysis of some marls used for Portland cement making:

TABLE XIII.—ANALYSES OF MARLS USED FOR MAKING PORTLAND CEMENT.

Used by	Silica, SiO_2.	Alumina, Al_2O_3.	Iron Oxide, Fe_2O_3.	Carbonate of Lime, $CaCo_3$.	Carbonate of Magnesia, $MgCO_3$.	Sulphur Trioxide, SO_3.	Organic Matter.
Bronson Portland Cement Co., Bronson, Mich	1.75	1.57		87.92	0.92	0.15	7.50
Wolverine Portland Cement Co., Coldwater, Mich	0.52	0.51	0.53	92.25	2.87	0.89	....
Omega Portland Cement Co., Mosherville, Mich	0.91	0.29		93.12	2.98	0.31	2.13
Peninsular Portlant Cement Co., Woodstock, Mich	0.38	0.68		90.66	1.81	trace	....
Detroit Portland Cement Co., Fenton, Mich.............	0.48	0.17	0.51	93.25	3.88	0.55	....
Empire Portland Cement Co., Warners, N. Y...........	0.50	0.20	0.10	96.16	1.20	0.80	1.04

Clay.

Clay consists of a mixture of kaolin with more or less sand and other impurities. Kaolin, sometimes called kaolinite, is a hydrated silicate of alumina, having the symbol $Al_2O_32SiO_22H_2O$. Sand is composed of grains of quartz and other minerals. Clay contains silica both as chemically combined silica in kaolin and the other minerals, and in the free state as quartz sand. Clay also contains more or less iron oxide, lime and magnesia and smaller quantities of potash and soda. Clay originates from the disintegration of rocks containing minerals made up largely of alumina and silica. The most abundantly occurring of these minerals are the feldspars, augite and hornblende. Nephelite and sodalite occur also to a much smaller extent. Decomposition takes place by the gradual leaching out of the more soluble elements of the minerals by water, leaving behind the less soluble ones, silica and alumina, together with smaller proportions of lime, magnesia, iron, potash and soda. These insoluble portions are washed over and over again and deposited in favorable places by water. Such deposits are called sedimentary clay, while clay which, instead of being washed away by water, is left near the rocks from whose decomposition it was formed is called residual clay. The potter deals more particularly with the plasticity, permanence when burnt and refractoriness of clay, but to the Portland cement manufacture these properties are of very secondary importance. The main thing, of course, is the chemical composition and the state of subdivision in which the silica exists. Roughly speaking, the clay should contain at least 2.3 times as much silica as alumina. Iron may replace alumina to almost any extent without detriment to the cement made therefrom. Magnesia and lime are usually present only in small quantities, the more of the latter present the better, but the former should be low, (not over 3 or 4 per cent.). The alkalies should not run over 3 per cent., as an excess is likely to cause unsound and quick setting cement.

Most clays will meet with the above requirements, the usual point to be looked into most carefully is the condition of the silica. All clay contains some uncombined silica, present as quartz sand or pebbles. The latter may be separated from the clay by mechanical means so the former is the one which gives most trouble. The sand must be present in the clay in a very finely divided condition. If much (over 5%) is present in the form of grains not passing a 100-mesh sieve, the clay is unsuited to cement manufacture. Under the section on "Analysis of the Raw Materials" a method is given for determining the quartz sand failing to pass a 100-mesh test sieve.

Below are some analyses of clays used in making cement:

TABLE XIV.—ANALYSES OF CLAYS USED FOR THE MANUFACTURE OF PORTLAND CEMENT.

Used by	Silica, SiO_2.	Alumina, Al_2O_3.	Oxide of Iron, Fe_2O_3.	Lime, CaO.	Magnesia, MgO.	Sulphuric Anhydride, SO_3.	Loss on Ignition.	Used with.
Alpena Portland Cem. Co., Alpena, Mich ..	61.09	19.19	6.78	2.51	0.65	1.42	5.13	Limestone
Bronson Portland Cem. Co. Bronson, Mich..	63.75	16.40	6.35	2.40	1.42	0.14	6.89	Marl
Buckeye Portland Cem. Co., Harper, O......	52.0	17.0	5.0	20.0	....	1.0	3.2	Marl
Catskill Cement Co., Smiths Landing, N.Y.	61.92	16.58	7.28	2.01	1.58	trace	....	Limestone
Glenn's Falls Port. Cem Co., Glenn's Falls, N.Y	55.27	28.15		5.84	2.25	0.12	....	Limestone
Newago Portland Cem. Co., Newago, Mich..	55.84	8.90	3.02	9.98	5.16	....	13.68	Marl
Pacific Portland Cem. Co., Suisun, Cal	58.44	18.95	7.55	1.70	1.88	....	9.07	Limestone

Shale.

For practical cement making purposes shale may be looked upon as merely solidified clay, since the chemical composition of the two are very similar and the same regard must be had as to the state of subdivision of the free silica. Shale is preferable to clay for mixing with limestone since segregation of the two is less likely to take place. It also carries less water and consequently does not require so much drying before grinding. Clays on the other hand are better suited to mixing with marls because of the similarity in physical properties between the two. If a mixture of dry clay and coarsely ground limestone is poured from a spout into a pile the clay will remain in the center of the pile and the limestone will roll down the sides of the pile. Now, if this pile is tapped from below in the middle, as it would be in a bin, the first material drawn would be most of it clay, while the last of it would be practically all limestone. To overcome this tendency to segregate, therefore, it is best to mix substances of like physical characteristics, shale with limestone and clay with marl.

Table XV gives some analyses of shales used in the manufacture of Portland cement:

TABLE XV.—ANALYSES OF SHALES USED FOR THE MANUFACTURE OF PORTLAND CEMENT.

Used by	Silica, SiO_2.	Alumina, Al_2O_3.	Oxide of Iron, Fe_2O_3.	Lime, CaO.	Magnesia, MgO.	Sulphuric Andydride, SO_3.	Loss on ignition.	Used with.
Hudson Portland Cem. Co., Hudson, N. Y.	62.39	20.26	7.31	0.33	1.49	....	8.03	Limestone
Southern States Portland Cement Co., Rockmart, Ga	57.35	21.18	3.77	4.85	2.00	....	7.10	
Coldwater shales in use by several Michigan mills	62.10	20.09	7.81	0.65	0.96	0.49	7.90	

Blast Furnace Slag.

In 1897 the Clinton Cement Co. in connection with the Clinton Iron and Steel Co., erected a small plant for the manufacture of Portland cement from limestone and slag, at Pittsburg, and in 1900, the Illinois Steel Co. began the manufacture of Portland cement from blast furnace slag and limestone at their South Chicago works. This plant has a capacity of 1500 barrels a day. The company has also under construction at this writing a larger plant, known as its Buffington plant, at Indiana Harbor, Ind., south of Chicago, and one at the Carnegie Steel Works, at Pittsburg. The Buffington plant which is nearing completion will have a capacity of about 4000 barrels a day.

There are two kinds of cement made from blast furnace slag and the two must not be confused, one a *true Portland* made by mixing limestone and slag, grinding very finely the resulting mixture and then *burning* just as if the raw materials were clay and limestone or cement-rock and limestone; the other a puzzolan or slag cement made by grinding with slaked lime suitable slag, which has been previously chilled suddenly by dropping into water. The resulting mixture is then ready for use and is not burned.

At the Illinois Steel Company's South Chicago plant the slag is granulated by cooling it suddenly with water, dried, ground, and then mixed with the proper proportion of ground limestone.

Slag suitable for the manufacture of Portland cement can only come from furnaces working on pure ores, such as those of the Lake Superior mines, and fluxed with low magnesian limestone. Generally speaking, the slag must analyze within the following limits:

Silica, plus Alumina, not over 48 per cent.
Iron and Alumina, 12 to 14 per cent.
Magnesia, under 3 per cent.

There is a slight thermal advantage in using slag for the manufacture of Portland cement. The lime is present as oxide, just as it is in cement, and no heat is required to decompose, as is the case with limestone where heat is required to change the carbonate to oxide.

This advantage, however, is negatived to some extent by the necessity of driving off the water used to granulate the slag. Even were this latter not the case, under the present wasteful system of burning cement, this saving would hardly be appreciable.

Below is an analysis of a typical slag used by the Illinois Steel Co. in making their "Universal" Portland cement.

Silica	33.10
Iron Oxide and Alumina	12.60
Lime	49.98
Magnesia	2.45

Alkali Waste.

The precipitated calcium carbonate obtained from the manufacture of caustic soda by the Leblanc process has been used successfully in Europe for the manufacture of Portland cement. The Michigan Alkali Co., Wyandotte, Mich., however, in 1899, built a small plant designed to take care of 100 tons of waste. This plant has now been leased to the Wyandotte Portland Cement Co., which uses limestone in place of the alkali waste so that the presumption is that the process did not pay. It seems hardly likely that alkali waste will be used again in this country in view of the availability of much more suitable materials. Those who are interested in the process, however, will find a paper of some length on the subject in "Cement and Engineering News" of March and April, 1900.

Below is an analysis of the alkali waste used by the Michigan Alkali Co.:

	Per cent.
Silica	0.60
Alumina and Iron Oxide	3.04
Carbonate of Lime	95.24
Carbonate of Magnesia	1.00
Alkalies	0.20

Gypsum.

Gypsum either in its native state or after calcining is always added to Portland cement to regulate the set for reasons which will be explained in Chapter XV, and hence may be considered as one of the raw materials of its manufacture. It consists of hydrated sulphate of lime, $CaSO_4.2H_2O$. This is usually contaminated by the presence of more or less silica, iron and alumina, carbonates of lime and magnesia, organic matter and sulphides. Gypsum is found in many localities in this country and in Nova Scotia and New Brunswick. From the latter places it is largely imported for use in the cement trade, for making wall plaster, plaster of Paris, etc.

When gypsum is heated to 132° C it loses three-fourths of its water of crystallization and another hydrate is formed having the formula $(CaSO_4)_2.H_2O$ and commonly known as plaster of Paris or calcined plaster. If gypsum is heated to a temperature of 343° C all the water is driven off and it is converted to anhydrite which has the formula $CaSO_4$, and is known usually as dead burned plaster.

Either gypsum or plaster of Paris may be used to slow the set of cement. If the retarder is to be added to the clinker before the latter is ground gypsum is usually used. If the addition is to be made at the stock house, when the cement is being packed, finely ground plaster of Paris is used. In valuing gypsum or plaster of Paris for cement manufacture the main requisite is the quantity of sulphate of calcium or SO_3 it contains, and the purchaser has to take into consideration chiefly how much of this he is getting for his money. In the case of plaster of Paris its fineness should also be taken account of, if it is to be added to ground cement. The finer the plaster, the better it is for this purpose.

A cement mill manufacturing 1000 barrels a day will use about 4 tons of gypsum or plaster per day. This is usually purchased from some dealer and arrives at the mill in bags, the gypsum being crushed to pass an inch perforated screen.

Below are the analyses of some gypsums used in retarding the set of Portland cement:

TABLE XVI.—SHOWING ANALYSIS OF SOME GYPSUMS USED IN THE MANUFACTURE OF PORTLAND CEMENT.

From	SiO_2.	$Al_2O_3 + Fe_2O_2$.	$CaCO_3$.	$MgCO_3$.	$CaSO_4$.	H_2O.
Nova Scotia...........	0.10	0.04	0.56	0.11	78.51	20.90
Michigan	1.31	0.64	2.27	0.18	76.83	20.01
Kansas	1.18	0.15	0.36	0.52	78.04	19.98
New York	2.11	0.61	1.18	0.65	76.51	19.36
Ohio	0.68	0.16	...	....	78.08	20.14

The Valuation of Raw Materials.

In passing on the availability of raw material for cement manufacture, a number of things must be considered besides mere analysis. The cost of quarrying or excavating, the power required to grind and the coal it will take to burn it must be considered. With excavating we include also cost of conveying to the mill. Marl and clay are the easiest raw materials to excavate, but on the other hand the mill can seldom be located near the beds of the former, owing to the necessity of having the mill located on firm dry ground. This necessitates pumping or carrying the marl, in some instances several miles and increases the cost of manufacture. A very shallow marl bed can not be worked as economically as a deep one because of the constant moving about of the excavating apparatus, etc. When the marl beds are located in the north, cold weather is apt to tie them up by the freezing of the lake over them, necessitating either the cutting of the ice or the shutting down of the mill. Both add to the cost of production. Cement-rock is usually blasted down, loaded on cars and hauled by cable to the mill, close at hand. It costs more in powder and drilling than marl, but, if a steam shovel is used to load the cars, costs less after it is down to convey to the mill than marl, as only half as much material has to be handled owing to the water in the marl. Even when loaded by hand the cost of quarrying cement-rock is no greater than that for marl. A recent writer[1] places the cost of excavating marl at 21 cents a ton, while the writer knows of several mills where the delivery of cement-rock to the crushers is done at a smaller figure than this. Limestone is harder than cement-rock and costs more to drill, blast and break up the lumps into sizes suitable for loading on the cars or carts. Shale will cost about the same as cement rock to quarry and load, but the mill is usually located near the limestone deposit or marl beds, as much more of these are needed, consequently the shale must usually be carried some distance to the mill. The cost of getting out either cement-rock or limestone will be influenced by the amount of "stripping" that has to be done. In some mills this top can be used, in which case this cost is saved.

Marl and clay are the easiest materials to grind, shale, cement-rock and chalky limestone come next, while limestone and slag are harder still. Slag is brittle but hard, breaks up to a size passing a 20-mesh sieve easily, but requires considerable additional grinding to make 95 per cent. of it pass a 100-mesh sieve.

Cement rock-limestone mixture burns easiest of any of the combinations in the kilns, limestone-clay, and slag-limestone mixtures are harder still and the wet marl and clay mixture requires much more coal than any other. In this case, burning and drying are considered together. Cement rock seldom contains more than 5% moisture and limestone even less as it comes from the quarry. Slag may carry 15 or 20 per cent. of water left in from the process of granulation, and marl 50 to 60 per cent. The more intimate

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[1] Soper, Cement and Engineering News, Feb., 1894.

mixture of the argillaceous and calcarious elements of the cement rock-limestone mixture makes it easier to burn than the equally dry limestone-clay combination, while the large quantity of water to be driven off in the kilns makes the burning of the marl-clay combination so costly. If marl and clay are introduced into the kiln dry they require no more fuel to burn than the cement rock limestone combination. The subjects of burning and grinding are treated of to greater length in special chapters and they should be consulted for data relative to the cost of manufacturing Portland cement from various kinds of raw material.

Portland cement can be made from such a variety of materials that almost every geological report will show analyses of hundreds of limestones, clays, shales and marls suitable for the manufacture of cement.

The mere fact therefore that raw materials of suitable chemical composition for the manufacture of Portland cement exists in a certain locality is no occasion for the erection of a mill on this site, because the success of the enterprise will depend more upon local conditions than upon the raw materials themselves. The cost of fuel, labor and supplies must be taken into consideration as well as the ability to market the product. The fuel item in the manufacture of Portland cement is a big one, dry material requiring from 165 to 200 lbs. of fuel per barrel of cement and wet material from 200 to 250 lbs., under the usual system, for burning and grinding.

Portland cement is so bulky in proportion to its value that the nearness of the mill to the market is also an important item.

The Lehigh District is blessed with a soft easily ground cement rock, but it probably owes its development also to cheap coal and labor, experienced men and its proximity to such markets as New York, Philadelphia and Boston.

CHAPTER IV.

PROPORTIONING THE RAW MATERIAL.

While a glance at the table of analysis on page 16 will show wide variation in the chemical composition of Portland cement, it must not be supposed that such latitude in proportioning the raw materials really exists. If the resulting Portland cement is to be sound, normal setting, and of good strength, it is imperative that the raw materials shall be correctly proportioned, as to the balance between the silica and alumina on the one hand and the lime on the other. Cements from different mills often vary several per cent. from each other as to the silica, lime and alumina, and yet one appears as good as the other. This variation is often due in part to addition of gypsum to, and the contamination by the coal ash of the clinker and also to the absorption of carbon dixoide from the air. It is still, however, evident that this will not account for all the variations, and that the raw mixtures from which cement is made vary widely, within certain limits, at the different works. Many attempts have been made to put the calculation of cement mixtures on a strictly scientific basis. So far as the work at the same mill is concerned, this has been successful; and it is comparatively easy, after a little observation and experimenting, to formulate a rule which will hold good for the mill in question; but when it comes to putting this into practice elsewhere, failures may result. Unquestionably as our knowledge of the constitution of Portland cement increases and our knowledge of the role played by the alkalies, iron, etc., during clinkering becomes more certain, we will be able to work out with mathematical precision the composition of cement mixtures.

Michaelis, Sr., Le Chatelier and Newberry have all proposed formulas for the correct proportioning of the raw materials.

Dr. Michaelis[1] bases his formula on, what he calls, the "hy-

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[1] Cement and Engineering News, August, 1900.

draulic modulus," a factor representing the ratio between the percentage of lime and the combined percentages of silica, alumina and iron oxide present in Portland cement. He states that this ratio must lie within the limits of 1.8 and 2.2 and proposes the empirical figure 2. His formula stated in the form of an equation is—

$$\frac{\%\ \text{Lime}}{\%\ \text{Silica} + \%\ \text{Iron Oxide} + \%\ \text{Alumina}} = 2$$

The writer has found this formula will in some instances give a mixture which would result, when burned, in a very much over-clayed, underlimed and consequently quick-setting cement. It does not seem to be applicable to all conditions. Of four cements analyzed by the writer recently, each from a different mill, the ratios were: A. 1.92, B. 2.01, C. 2.07, D. 2.18. Any cement made at mill D with this formula would have been decidedly quick-setting. When the contamination of the cement by the fuel ash is taken into consideration it is probable that A is the only one of these four cements in which the ratio between the lime and the silicates before burning was 2.

Newberry followed up his paper on the constitution of Portland cement, mentioned in Chapter II, with the first formula, based on scientific rather than empirical knowledge, of which the writer knows. Considering cement to be composed of tricalcium silicate, $3CaO.SiO_2$, containing 2.8 times as much lime as silica, and dicalcium aluminate, $2CaO.Al_2O_3$, containing 1.1 times as much lime as alumina, he proposed the following:

$$\text{Lime} = \text{silica} \times 2.8 + \text{alumina} \times 1.1$$

or

$$\text{Carbonate of Lime} = \text{silica} \times 5 + \text{alumina} \times 2.$$

As this formula represents the maximum of lime which a cement could carry, if it were manufactured under ideal conditions as to grinding and burning, conditions which are never met with in practice, he found it necessary in actual work to carry the lime a little lower than that called for by the formula, say between 95 and 98 per cent. of the maximum. Ninety-five per cent. of the maximum would give the following:

$$\text{Carbonate of Lime} = \text{silica} \times 4.8 + \text{alumina} \times 1.9.$$

As an example of the method of using the formula let us suppose we wish to make a cement mixture from limestone and cement rock of the following composition:

ANALYSES.

	Cement Rock.	Limestone.
Silica	19.06	2.14
Iron Oxide	1.14	.46
Alumina	4.44	1.00
Carbonate of Lime	69.24	94.35
Carbonate of Magnesia	4.21	2.18

The calculation is as follows:

LIMESTONE.

Total carbonate of lime		94.35
Silica,	$2.14 \times 4.8 = 10.27$	
Alumina,	$1.00 \times 1.9 = 1.90$	12.17
Available carbonate of lime		82.18

CEMENT ROCK.

Silica,	$19.06 \times 4.8 = 91.49$	
Alumina	$4.44 \times 1.9 = 8.44$	
		99.93
Less carbonate of lime contained		69.24
Required carbonate of lime for 100 parts		30.69

The number of parts of limestone required for 100 parts cement-rock will then be

$$\frac{30.69 \times 100}{82.18} = 37.3$$

37.3 lbs. limestone contain		35.19 lbs. $CaCO_3$
100.0 " cement rock "		69.24 " "
137.3 " mixture		104.43 " "

Mixture should, therefore, analyse:

$$\frac{104.43 \times 100}{137.3} = 76.0\ \%\ \text{carbonate of lime}$$

A table[1] for saving the multiplication in this calculation is

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[1] Meade, Cement and Engineering News, December, 1901.

shown in Fig. 1. It is made of cross-section or co-ordinate paper, such as can be bought by the sheet or yard from any dealer in draughtsman's supplies. The paper ruled in squares every centimeter with broad lines and these spaces divided again into tenths by fine lines is best for this use. A sheet of this of sufficient size to cover all raw material used in the particular plant is either pasted to a sheet of stiff card board or tacked to a drawing board. After drying, the large divisions on the lower margin are numbered 1, 2, 3, etc., to correspond to the percentages of silica and alumina in the clay, while the divisions of the same size on the right and left hand margins are numbered 5, 10, 15, etc., to correspond to pounds of calcium carbonate. Now two lines are drawn, one making an angle of 45° with the horizontal margin

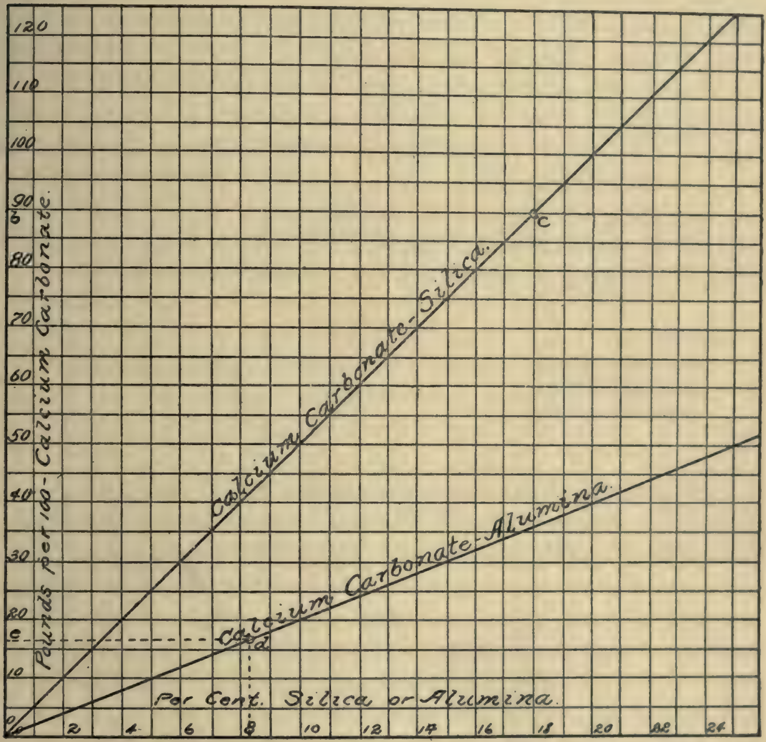

Fig. 1. Graphic Method of Proportioning Cement Mixture.

and passing through the O, O point, the other passing through the same O, O point but making an angle of 21°, 48′. The first line represents the "calcium carbonate-silica" ratio and should be so designated, the second the "calcium carbonate-alumnia" ratio. The abscissas (figures on the lower margin) of points on the calcium carbonate-alumina line represent the percentage of silica in the cement-rock and the ordinates (figures on the side margins) the corresponding weight of calcium carbonate. Similarly the abscissas of points on the calcium carbonate-alumina line express the percentage of alumina and the ordinates of these points the corresponding weight of calcium carbonate. As an example, to explain the use of the table, suppose we wish to know how much calcium carbonate to mix with a rock of the composition:

	Per cent.
Silica	18.0
Alumina, etc	8.3
Calcium carbonate	67.3
Other constituents	5.9
	100.00

First find the calcium carbonate equivalent to the silica in the stone. To do this run up the vertical line corresponding to 18 to *"c"* where it cuts the line marked "calcium carbonate silica." The ordinate *"b"* of this point, (found by running along the nearest horizontal line to *"c"* to the margin) or 90, will be the weight of calcium carbonate equivalent to the silica. Next find the calcium required for the alumina by running up the vertical line corresponding to 8.3 to *"d"* where it cuts the line marked "calcium carbonate-alumina" and then along the nearest horizontal line to this point to the side margin. The reading here *"e"* or 16.6 will be the weight of calcium carbonate required for the alumina. The silica and alumina together of course will require 16.6 + 90 or 106.6 pounds of calcium carbonate, but since the cement rock contains 67.3 per cent. calcium carbonate it is only necessary to add to it 106.6 — 67.3 or 39.3 pounds of calcium carbonate.

It is not necessary to use a protractor in drawing the "calcium carbonate-alumina" and the "calcium carbonate-silica" lines. It is evident that both lines must pass through the O, O point. Any other point through which they must pass may be quickly found by calculation and the lines drawn through these two points. For example 25 per cent. silica will require 25x5 or 125 pounds of calcium carbonate. So if the line "calcium carbonate-silica" is drawn through the O, O point and the point of intersection between the vertical line corresponding to 25 per cent. silica and the horizontal line corresponding to 125 pounds of calcium carbonate, it will have the proper angle. Similarly the alumina line should be drawn through the O, O point and that of the intersection of the vertical line corresponding to 25% alumina and the horizontal line corresponding to 25x2 or 50 lbs. of calcium carbonate.

The substitution of any other lime-silica and alumina ratio than that represented by Newberry's formula can easily be effected. For example let us suppose that in a given plant Newberry's formula gives an "overlimed" cement, and that a formula

$$\text{Calcium carbonate} = \%\ \text{silica} \times 4.9 + \%\ \text{alumina} \times 1.96$$

gives better results. Then in order to express this ratio it is necessary to draw the silica line through the O, O point and the point of intersection of the vertical line representing 25% silica and the horizontal line representing 25x4.9 or 122.5 pounds calcium carbonate. The alumina line is drawn through the O, O point and that of the intersection of the vertical line representing 25% alumina and of the horizontal line 25x1.96 or 49.0 pounds calcium carbonate.

Nothing will be gained by having the larger divisions of the coordinate paper represent less than one per cent. silica or alumina and five pounds of calcium carbonate, since the small spaces will then represent 0.1 per cent. and technical determinations of lime, silica and alumina are seldom nearer the truth than this. This will keep the tables well down in size. When used with clays high in silica space can be saved my having two tables—one ranging say from 10-25% and serving for the alumina in the clay and the alumina and silica in the marl, the other ranging say from 45 to 60% for the silica in the clay. In these tables two points must of course be determined. In the first the silica line would of course pass through the point of intersection of the vertical and horizontal lines representing 10% silica and 10x5 or 50 pounds calcium carbonate, respectively, and the point of intersection of the vertical and horizontal lines representing 25% silica and 25x5 or 125 pounds of calcium carbonate, respectively. While in the second table it would pass through the points of intersection of the vertical line representing 45% silica and the horizontal line representing 45x5 or 225 pounds of calcium carbonate, and of the vertical line corresponding to 60% silica and the horizontal line corresponding to 60x5 or 300 pounds calcium carbonate.

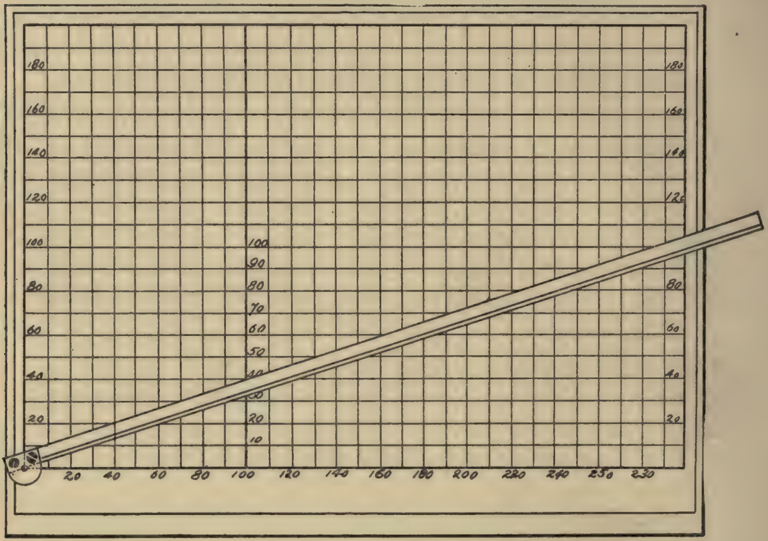

Fig. 2. Graphic Method for Calculating Limestone.

The lines may of course be drawn to represent the lime, calcium oxide, required; in which event the main vertical divisions should be numbered 2, 4, etc., and have twice the value of the spaces on the horizontal margin. The silica line would in this event be drawn through the O, O point and the point of intersection of the vertical line corresponding to 25% silica and the horizontal line corresponding to 25x2.8 or 70 pounds calcium oxide.

The above table shows us merely the amount of pure carbonate of lime required by the cement-rock clay or shale. To find the limestone necessary it is of course necessary to find the available carbonate of lime it contains by the above chart and then calculate the quantity to be added as shown on page 54. The following table, Fig. 2, will save this calculation also, however. A large piece of co-ordinate paper is fastened to a board and the main divisions on the lower margin are numbered 10, 20, 30, 40 etc., to correspond to pounds of limestone. Those on the right and left hand margins are numbered 10, 20, 30, 40, etc., and represent pounds of calcium carbonate required for the cement rock. On the vertical line 100, the main divisions are numbered 10, 20, 30, etc., to represent pound per 100 or percentage of *available* calcium carbonate in the limestone. A ruler is fixed so as to turn about the O, O point. The pivot around which the rules moves must be on a line with the edge of the ruler. It is only necessary to set the edge of the ruler at the point on the 100 vertical line (This line is in the drawing made broad but it would be better to rule over it or to one side in red ink.) representing the percentage of *available* calcium carbonate in the limestone. The edge of the ruler is then used as if it were a diagonal line.

To find the number of pounds of a limestone equivalent to a given weight of calcium carbonate, glance along the horizontal line corresponding to the quantity of pure calcium carbonate required until it meets the ruler's *lower* edge. The corresponding reading at the lower margin will give the weight of limestone. For example, using the table, we wish to know how much of a limestone containing 32.5 pounds available $CaCO_3$ is required for a cement rock that requires 39.3 pounds calcium carbonate. Set the ruler's *lower* edge so it intersects the 100 vertical line at 32.5 and run the eye along the horizontal line corresponding to 39.3 to where it cuts the diagonal line which passes the 100 vertical line at 32 (or 33), and then down the nearest vertical line to the margin, the reading here, or 121, will be the weight of limestone needed.

The writer has used in his work a formula modeled after Newberry's, which is given below. It assumes 90 per cent. of the theoretical lime needed to form tri-calcium silicate and tri-calcium aluminate.

$$\left.\begin{array}{l}\text{Limestone needed per ton or per}\\ \text{pound of cement rock (or clay)}\end{array}\right\} = \frac{(A_1 \times 4.5 + B_1 \times 2.7) - C_1}{C_2 - (A_2 \times 4.5 + B_2 \times 2.7)}$$

When

A_1 = percentage SiO_2 in the cement rock or clay
B_1 = “ Al_2O_3 in the cement rock or clay
C_1 = “ $CaCO_3$ in the cement rock or clay
A_2 = “ SiO_2 in the limestone or marl
B_2 = “ Al_2O_3 in the limestone or marl
C_2 = “ $CaCO_2$ in the limestone or marl

Cement mixtures proportioned by this formula will be neither over nor underlimed and the resulting cement, if properly burned, will give good strength and soundness tests.

This will be found as near a general formula, applicable to all cases and material, as it is possible to get, in the present state of our knowledge of the constitution of Portland cement clinker.

Fixed Lime Standard.

While Newberry's formula is very useful for calculating cement mixtures from complete analyses, as in making laboratory trial burnings, or when starting up a new mill, or opening a new deposit, it will be found more practicable in actual mill routine work, to fix upon a certain percentage of carbonate of lime found to give satisfactory results by experience and to keep the mixture as near this as possible. Provided the amount of water, organic matter and magnesia is constant in raw materials, it will be comparatively easy to keep a pretty uniform mixture by merely watching the percentage of carbonate of lime. In the cement-rock-limestone mixtures of the Lehigh District the conditions are pretty constant and it is the usual practice here to "control the mix" by keeping the percentage of carbonate of lime in it around a fixed point (usually 74.5 to 75.5) the standard varying at different mills. In most mills using limestone-clay mixtures, very much the same conditions obtain, the magnesia and water remaining fairly constant and organic matter being present only in very small percentages. Some clays show considerable variations in different parts of the bed in the relative proportions of the silica and the alumina to each other. In this event the clay should be so worked as to give a constant ratio between the silica and the alumina. By doing this a constant lime standard may be held to, and a cement of more uniform setting properties will result. In the marl-clay mixtures water and organic matter are apt to vary widely, and in order to make a uniform mix it is necessary to do more than merely determine the lime in the slurry, as the wet mixture of marl and clay is called. When the organic matter is constant it is merely necessary to dry the mixture and determine the carbonate of lime as in a limestone-cement rock or limestone-clay mixture. In controlling the mixture by a carbonate of lime determination it is necessary that the ratio between the silica and alumina be kept constant, this can usually be done without difficulty after a thorough prospecting of the raw materials. This problem will usually be simplified by having the quarrying operations spread out over the whole face, and on several ledges, and not confined to one particular spot. For instance, suppose a quarry to have a face of 100 ft. and a depth of 48 ft. and to be worked in benches of 16 ft. each. It will be a simpler matter to keep a constant ratio between the silica and the alumina by distributing the quarry force over the whole face taking rock from several benches than it would be by localizing the work with a steam shovel at one point.

Formulas for a Fixed Lime Standard.

The mathematical part of calculating cement mixtures for a fixed lime standard may be simplified by the following formulas, which have been used by the writer in his work and found useful.

The first formula is for use when the cement rock is weighed and the proper proportion of this weight of limestone is added.

1. To find the percentage of a given limestone to be added to a given cement-rock or clay to make a given mixture

Let—

X = Percentage of limestone necessary.
L = Percentage of $CaCO_3$ in the Limestone.
R = Percentage of $CaCO_3$ in the Rock or Clay.
M = Percentage of $CaCO_3$ desired in the Mixture.

Then—

$$X = \frac{M - R}{L - M} \times 100$$

Example—What percentage of limestone analyzing 95 per cent. $CaCO_3$ must be added to a cement rock analyzing 70 per cent. $CaCO_3$ to give a mix analyzing 75 per cent. $CaCO_3$?

$$\text{Percentage of limestone} = \frac{75 - 70}{95 - 75} \times 100 = \frac{500}{20} = 25$$

Hence, to every 100 lbs. of cement rock 25 lbs. of limestone must be added.

The next formula is practically the same as the last only it is intended for use when the limestone or marl is weighed and the proper proportion of this weight of clay or shale is added.

2. To find the percentage of a given clay or shale (or cement rock) to be added to a given marl or limestone to make a given mixture.

Let—

X = Percentage of Clay or Shale necessary.
C = Percentage of CaO in Clay or Shale.
L = Percentage of CaO in Marl or Limestone.
M = Percentage of CaO desired in the mixture.

Then—

$$X = \frac{L - M}{M - C} \times 100$$

Example—What percentage of clay analyzing 2.5 per cent. CaO must be added to a limestone containing 53 per cent. CaO to obtain a mixture analyzing 41.0 per cent. CaO?

$$\text{Percentage clay} = \frac{53 - 41}{41 - 2.5} \times 100 = \frac{1200}{38.5} = 31$$

Instead of percentages of CaO percentages of $CaCO_3$ may be used, but if used in one case, it must be used in all.

It sometimes happens that it is more convenient to divide the mix into percentages of limestone and of cement rock or clay than to make one constituent a certain percentage of the other. For example, when both the limestone and cement rock are already in storage and both are weighed into the same hopper, it makes fewer dumps necessary, to fill the hopper full each time and to so proportion the limestone and clay as to just do this. The following formula will give the percentage of both the calcarious and argillaceous constituents of the mixture.

3. To find the percentage of a given cement rock and of a given limestone for a given mix.

Let—

X = Percentage of Cement Rock, Shale or Clay.
Y = Percentage of Limestone or Marl.
R = Percentage of $CaCO_3$ in Cement Rock, Shale or Clay.
L = Percentage of $CaCO_3$ in Limestone or Marl.
M = Percentage of $CaCO_3$ desired in Mixture.

Then—

$$Y = \frac{M - R}{L - R} \times 100$$

$$X = \frac{L - M}{L - R} \times 100$$

$$\text{or } X = 100 - Y$$

$$Y = 100 - X$$

Example—What percentage of limestone analyzing 95 per cent. $CaCO_3$ and of cement rock analyzing 70 per cent. $CaCO_3$ are required in a mixture to analyze 75 per cent. $CaCO_3$?

$$\text{Percentage limestone} = \frac{75 - 70}{95 - 70} \times 100 = \frac{500}{25} = 20$$

$$\text{Percentage cement rock} = \frac{95 - 75}{95 - 70} \times 100 = \frac{2000}{25} = 80$$

To illustrate a case where these formulas are applicable, let us suppose that our hopper holds 10,000 lbs., then 10,000 × .20 or 2,000 lbs. of this must be limestone and 10,000 × .80 or 8,000 lbs., must be cement rock.

As another example, let us suppose that at a four kiln plant there are say six men wheeling limestone and cement rock from separate piles to the crusher, and that each barrow holds a maximum of 500 lbs., while the six in rotation per trip usually handle 2,500 lbs. Now, 20 per cent. of 2,500 lbs. is, of course, 500 lbs., and 80 per cent. is 2,000, so that there must be 500 lbs. of limestone for every 2,000 lbs. of cement rock. By putting two men on the limestone pile and setting their scale at 250 lbs. and four men on cement rock with their scale set at 500 lbs., the mix will be kept in proper proportion.

After the mixture has been made and checked, if it is desired to correct that which has been already ground, the two formulas first given, as the case may require, may be used. If the mix analyzes too low and limestone is needed the first formula must be used. If too high and clay is called for the second formula will give the amount.

Unfortunately in many mills no provision is made for correcting the mix after it leaves the grinders and the efforts of the chemist are directed merely to making the subsequent mix all right. The formula given below is for use here and gives the correct amount of limestone for the new mixture.

4. *To calculate the correct percentage of limestone to be added to a cement rock from the result of a former mixture of the two.*

Let—

M = Percentage of $CaCO_3$ desired in mixture.
F = Percentage of $CaCO_3$ found in mixture.
A = Percentage of Limestone already added.
L = Percentage of $CaCO_3$ in Limestone.
X = Corrected Percentage of Limestone needed to make the mixture analyze M per cent. $CaCO_3$.

Then—

$$X = A + \frac{(M - F)\ (100 + A)}{L - M}$$

Example 1.—The mixture analyzes 74.5 and should analyze 75.0 per cent. $CaCO_3$. 20 per cent. (of the weight of the cement rock) of limestone analyzing 95 per cent. $CaCO_3$ was added. What amount should be added?

$$X = 20 + \frac{(75 - 74.5)\ 100 + 20)}{95 - 75} = 22 + \frac{0.5 \times 120}{20} = 20 + \frac{60}{20} = 23 \text{ per cent.}$$

Example 2.—The mixture analyzes 76.0 per cent. $CaCO_3$ and should analyze 75.0 per cent. $CaCO_3$. If 20 per cent. of 95 per cent. limestone has been added, to what should this be reduced?

$$X = 20 + \frac{(75 - 76)\ (100 + 20)}{95 - 75} = 20 + \frac{-1 \times 120}{20} = 20 - 6 = 14 \text{ per cent.}$$

Where clay is added to limestone or marl and where formula 2 has been used to calculate the mix then formula 4 becomes as follows:

5. *To calculate the correct percentage of clay or shale to be added to a limestone or marl from the result of a former mixture of the two.*

Let—

M = Percentage of CaO desired in Mixture.
F = Percentage of CaO found in the Mixture.
B = Percentage of Clay already added.
C = Percentage of CaO in Clay.
X = Corrected Percentage of Clay needed to make the mixture analyze M per cent. CaO.

Then—

$$X = B - \frac{(M - F)\ (100 + B)}{F - C}$$

When it is customary to divide the mix into percentages and where formulas No. 3 have been used to calculate the mix the formula given below will arrive at the corrected percentages of cement rock and of limestone.

6. *To calculate the correct percentage of limestone and of cement rock in a mixture from the result of a former mixture.*

Let—

M = Percentage of $CaCO_3$ desired in mixture.
F = Percentage of $CaCO_3$ found in mixture.
A = Percentage of Limestone already in mixture.
L = Percentage of $CaCO_3$ in the Limestone.
X = Corrected Percentage of Limestone to make the mixture analyze M per cent. $CaCO_3$.

Then—

$$X = A + \frac{(M - F)\ (100 - A)}{L - F}$$

$$Y = 100 - X$$

Example—The mixture analyzes 74.5 and should analyze 75.0. The mixture is composed of 20 per cent. limestone analyzing 95 per cent. $CaCO_3$, 80 per cent. cement rock. What are the correct proportions?

$$X = 20 + \frac{(75 - 74.5)\ (100 - 20)}{95 - 74.5} = \frac{0.5 \times 80}{20.5} = 21.95 = \text{about } 22$$

$$Y = 100 - 22 = 78$$

In formula No. 6 it is assumed that the percentage of $CaCO_3$ in the limestone is correct and that the error in the mix causing it to be 74.5 instead of 75.0 $CaCO_3$ is due to the failure to properly sample the cement rock. If clay is added to rock or limestone for the mixture it is better to assume the clay to be correct, in which case we have the following:

7. To calculate the percentage of clay or shale and of limestone or marl in a mixture from the result of a former mixture,

Let—

M = Percentage of CaO desired in Mixture.
F = Percentage of CaO found in Mixture.
B = Percentage of Clay or Shale already in Mixture.
C = Percentage of CaO in Clay or Shale.
Z = Correct Percentage of Clay or Shale in the Mixture to make it analyze M per cent. CaO.
X = Corrected Percentage of Limestone or Marl.

Then—

$$Z = B + \frac{(F - M)(100 - B)}{F - C}$$

$$X = 100 - Z$$

Example.—The mixture analyzes 40.5 and should analyze 41.0 per cent. CaO. The mixture is composed of 24 per cent. clay and 76 per cent. limestone. Clay analyzes 3 per cent. CaO. What are the correct proportions?

$$Z = 24 + \frac{(40.5 - 41.0)(100 - 24)}{40.5 - 3} = 24 + \frac{-0.5 \times 76}{37.5} = 24 - 1.0$$

$$= 23 \text{ per cent.}$$

$$X = 100 - 23 = 77$$

A slide rule will greatly facilitate rapid calculation of cement mixture and changes to be made in the same.

A 10-inch one can be bought for as little as $1.25 and will be found to come in very handy for other laboratory calculations where accuracy is not required to more than three figures, such as figuring out the percentage of sulphuric anhydride and magnesia in an analysis.

A simple table of the quotients of $\frac{100}{L - M}$ or $\frac{100}{M - C}$, which ever is used, will greatly aid calculations. Formula 1 will then become $X = (M - R)\ Q$ when $Q = \frac{100}{L - M}$, and formula 2 will be $X = (L - M)\ R$ where $R = \frac{100}{M - C}$. Below is given such a table for a mix desired to contain 75 per cent. $CaCO_3$, and for limestone ranging from 92 to 98 per cent $CaCO_3$.

Values of Q, Mixture = 75.0 per cent. $CaCO_3$.

Per Cent. $CaCO_3$ in Limestone.	Q	Per Cent. $CaCO_3$ in Limestone.	Q
92.0	5.9	95.5	4.9
92.5	5.7	96.0	4.8
93.0	5.6	96.5	4.7
93.5	5.4	97.0	4.5
94.0	5.3	97.5	4.4
94.5	5.1	98.0	4.3
95.0	5.0	98.5	4.2

Using this table in the example given under 1.

Percentage of Limestone = (75-70) × 5 = 25.

Controlling the Mixture in the Wet Process.

For controlling the mixture in mills using marl and clay and consequently the wet process, many methods are in vogue. At some of the plants the slurry is merely dried and the carbonate of lime determined in the usual manner as outlined in Chapter X, either by titration with standard *N/2* acid and alkali or by measuring the volume of carbon dioxide liberated in the Scheibler's calcimeter. Another plan and one which is in use in the laboratory of the Omega Portland Cement Co., Jonesville, Mich., is to determine the lime by titration with standard *N/2* acid and alkali, and also "the silicates." The determination of the latter is also given in the chapter on "The Analysis of the mix." The ratio between the silicates and the lime is then kept constant. In a sample of correctly proportioned slurry upon which this determination was made, the ratio was 3.8. This ratio undoubtedly will vary at different mills, and also with any variations in the manner of carrying out the determination of the silicates, so that this ratio must be fixed by experience. At a new mill it could be determined to some extent before beginning operations by making up a set of "standard samples" (using Newberry's modified formula to determine the proper proportions) from various lots of marl and clay. The marl for these samples should be so selected as to cover the range expected to be met with in practice. This applies to the clay also. The ratios between the lime and the silicates should then be determined and if found fairly constant it can be adopted. If possible these samples should be checked by burning in a small kiln and examining the properties of the resulting cement. It may be found necessary after starting up the mill to raise or lower this ratio.

At the two mills of the Sandusky Portland Cement Co., the mix is controlled by the ratio between the percentage of lime, determined by acid and alkali, and the percentage of "insoluble," as determined by boiling one gram for 5 minutes with 10 per cent. hydrochloric acid, filtering, washing, igniting and weighing. This ratio is also different for different works. At the Sandusky plant of the above company the ratio is about 3.9 and at the Syracuse, Ind., mill 4.2, the difference being due to a greater amount of carbonate of magnesia and a more silicious clay at the latter mill. This ratio must be fixed like the lime-silicate ratio by comparison with samples carefully analyzed.

The author suggests the following method of control as doing away with the uncertainties due to water and organic matter in the slurry. Measure into a large weighed platinum crucible such a quantity of wet slurry as will give about 0.8 gram of dried slurry (or that amount, 0.8 gram, direct of dried slurry). Dry rapidly, avoiding any large loss by spattering if necessary, ignite cautiously at first, then strongly for 5 minutes over a Bunsen burner, and then for 10-15 minutes over a blast. The result will be a clinker of practically the same composition as that obtained in the kiln except that it lacks the fuel ash. The crucible and contents are then weighed and the weight of the clinker calculated. The lime is then determined in this clinker by the rapid permanganate method given in Chapter IX. This gives an excellent check on the slurry, if the magnesia is anywhere near constant, as it is only necessary to keep the lime in this clinker around a constant figure. The sample of wet slurry may be rapidly dried, in the crucible, in the following manner: Incline the crucible on a tripod over a burner turned low, in such a way that the flame plays under the upper part of the crucible. This will cause a rapid evaporation of the water. When the mass looks dry the burner can be moved back gradually until it plays upon the mass directly and allowed to remain here 5 minutes when the crucible is ready for the blast. The lime will be somewhat higher in this artificially prepared clinker, than in that from the kilns, owing to the contamination of the latter by the fuel ash, and still higher in lime than the finished cement in which it is lowered by the addition of gypsum and the absorption of water from the air. What the lime should be in the clinker can easily be determined by applying the method to standard samples.

In making the mixture with wet materials such as clay and marl the water and organic matter are disturbing elements. In order to make the mixture with these materials it is necessary to determine the percentage of water they contain, and from this to calculate the weight of wet marl or clay equal to a given weight of dry material. For instance, suppose the marl to contain 60 per cent. water and the clay 15 per cent. Then 100 lbs. of wet marl would only contain 100-60 or 40 lbs. dry marl, and from the proportion

$$(40:100::100:X)$$

We find 250 lbs. of wet marl are equivalent to 100 of dry marl.

If 100 lbs. of dry marl require 31 lbs. of dry clay, it would require 36.4 lbs. of wet clay by a similar calculation. So that our proportions would be 250 of wet marl to 36.4 of moist clay.

This will apply to the use of any of the formulas given in this chapter, when used for calculations involving wet materials. The results will be in pounds of *dry* material and must then be calculated to wet marl, clay or slurry. In using the ratio between either the lime and the silicates or the lime and insoluble. The lime and the silicates must be found in the marl, and the silicates (and lime if any) in the clay, if the first method is used; and the lime and the insoluble in the marl, and the insoluble and lime, if any, in the clay, if the second method is to be used, in order to proportion the two. The following formula will give the proper proportions of clay and marl to make a slurry of a given ratio.

Let—

L = Lime in the Marl.
l = Lime in Clay.
S = Silicates (or Insoluble) in Marl.
s = Silicates (or Insoluble) in Clay.

$$R = \text{Ratio} = \frac{\text{Lime}}{\text{Silicate (or Insoluble)}}$$

Then—

$$\frac{\text{Marl}}{\text{Clay}} = \frac{R \times S - l}{L - R \times S}$$

This formula may, of course, be used to correct a slurry found to be too high or low in lime. In this event, if the clay is called for, the lime and silicates in the slurry should be represented by L and S, but if marl is needed, by l and s.

CHAPTER V.

QUARRYING, EXCAVATING, DRYING AND MIXING THE RAW MATERIAL.

Quarrying the Stone.

Limestone, cement-rock and shale are usually quarried, while clay is dug from pits and marl is dredged, often from under water. Deposits of cement rock and limestone are usually overlaid by a few feet of soil and clay which must be removed by scrapers or shoveling. When clay is used to make the mix, this surface deposit is conveyed to the mill, otherwise it is carted away to a dump. In one or two quarries, notably that of the Lawrence at Siegfried, Pa., it has been necessary to mine the stone, owing to the dip of the material, which carries down under other rock. This method rarely pays, however, as in order to meet competition, it is necessary to deliver the rock to the mill at a lower cost than will permit of mining. Some deposits of rock and limestone are so situated that they can be opened on a hillside, at others, it has been necessary to go straight down.

The stone is usally blasted down in benches, sometimes along the whole face of the quarry at once, at others, only a small part of a bench at a time. The drill holes for the blasting are usually made with power drills, run by steam or compressed air, and are carried to a depth of 16 to 20 feet. In blasting, an effort is made to shatter the rock as much as possible, in order to save subsequent sledging and blasting to break up the big pieces. In spite of this attempt it is necessary at practically all of the quarries, except that of the Edison Portland Cement Co., to break up some big pieces of rock either with dynamite or hand sledges. It seems curious, in this connection, that no one has tried the use of air hammers to do this work. They would be much cheaper than hand sledging and would undoubtedly break up the rock.

Where many large rocks have to be broken up by dynamite, a small hand air drill will be found more convenient for this purpose than anything else. These drills can be attached to a long piece of strong flexible hose coupled to the air line and used to drill rocks in any part of the quarry. In a minute's time a hole a foot deep can be drilled in cement rock, and this can then be filled with dynamite and the rock shattered.

After breaking up to a size suitable for crushing and loading, the rock is ready for the mill.

In some quarries the rock is loaded on carts and carried to a point out of danger from the blasting and dumped into side dump cars which are hauled to the mill up an incline by a cable hoist. At other mills, temporary tracks are laid from a turn-table or switch at the face of the incline to the rock piles, and the cars are loaded direct from these, and then hauled to the mill as before. When the quarrying has been carried straight down, the rock is loaded on skips, which are carried to the mill by an ærial cable and hoist. The cars are loaded by hand at nearly all cement mills and a great deal of sledging is necessary in order to reduce the rock to a size suitable for handling and crushing. At a few of the larger mills steam shovels are used, but they interfere to some extent with blasting and the crushers at most of the mills are too small to take the rock, as it comes from the pile, without being broken up. Then, too, unless the deposit is very regular the steam shovels localize the quarrying so that the cement is not so uniform as if a large face were worked. Nevertheless, it is probable that they will be introduced gradually, in connection with either larger crushers or some form of air or steam hammer to break up the large pieces of rock in the quarry, and that the chemist will be expected to work out a way around the difficulty of an irregular composition.

When the material is of a regular composition such as is often the case with limestone, shale or clay, steam shovels can be used to advantage and on the latter two classes of material are used to some extent. As clay is soft the steam shovel can both dig out the clay and load it on the cars. Usually it is necessary to carry the clay some distance, for the mill is always located as near the marl or limestone as possible, as four or five times as much of these are used as of clay or shale.

Excavating Marl.

Marl as has been said carries considerable water and the deposits usually lie in depressions and underneath the surface of a shallow lake or marsh. In some instances, the marl deposit is overlaid by a foot or more of peat which must be dredged off. In excavating the marl several plans are followed, one of the most common is that of a steam dredge mounted on a barge which scrapes up the marl from the bottom of the lake and loads it on barges. These barges are then towed to the wharf and unloaded by machinery on belt conveyors which carry the marl to the mill. This can, of course, be done only where the marl lies under water. When the beds have been drained, it is usual for the steam dredge or shovel to float on its barge, in the channel which it cuts out of the marl, and to load the marl on to cars, running on temporary tracks, on a bank by the barge. The channel fills with ground water and the bank is thrown up by the dredge either from the stripping on top of, or the material underneath the marl. Instead of using barges and cars to convey the marl to the mill some of the Michigan mills drop their marl from the scoop of the dredge into the hopper of a pug mill on a boat or car. Here the marl is mixed with water to form a thin mud, which is pumped to the mill through a pipe line, carried over the marsh or marl bed on a wooden trestle. The steam dredges are of the same type as those used for excavating cuts by railroads and for deepening the channels of rivers and harbors. They consist of a scoop or dipper having a hinged bottom and fixed to a long arm. This arm can be swung to either side, raised, lowered or pushed forward, by a system of chains, racks and pinions. Some of the dredges are of the orange peel bucket type. These have a bucket hanging from a revolving arm by cables or chains, which opens and shuts and is filled by lowering to the bottom of the lake open and then closing. Fig. 3 shows a steam dredge such as is used in excavating marl.

The pug mills, Fig. 4, used in cement works are similar to those used in the better equipped brick yards, and consist of a long steel cylinder, in which revolve two shafts provided with steel blades. The mixture of marl and clay enters at one end and is forced out at the other. During its passage it is churned up by

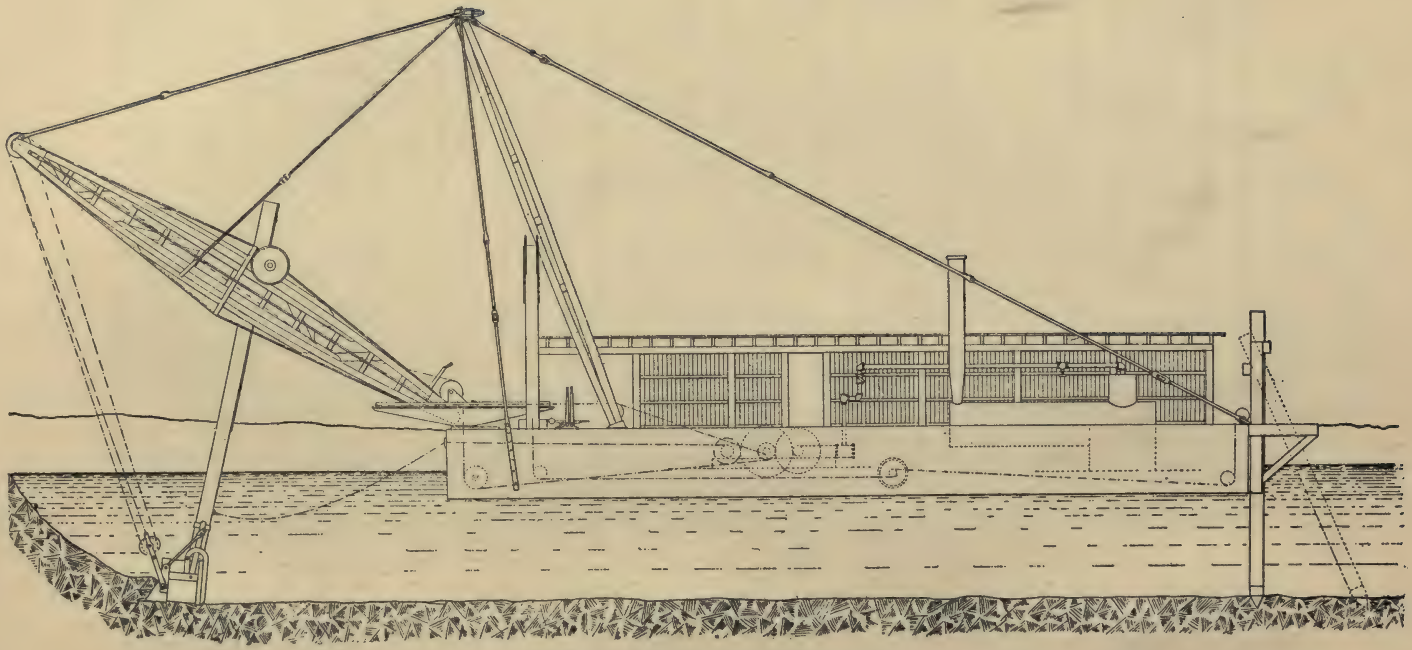

Fig. 3. Steam Dredge for Excavating Marl.

the blades and thoroughly mixed. When the marl is pumped from the lake to the mill, it is usual to locate a separator on the barge to take out the sticks, roots, etc. This consists usually of a perforated screen through which the marl is forced. The separator also serves as a pug mill in reducing the marl to a uniform paste.

The best system of pumping marl is with compressed air. In this system of pumping, there are two cylinders located side by side, both of which are connected with the air compressor. One of these cylinders is being drawn full of slurry by the compressor while the other is being emptied. When used for pumping marl to the mill the cylinders and air compressor are located on the barge. Fig. 5 shows this system and Fig. 6 illustrates a ball valve plunger slurry pump which was manufactured by the Bonnot Co. Its action is similar to that of other pumps and is evident from the cut.

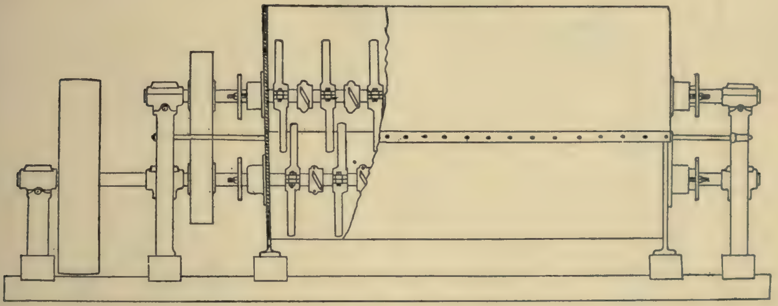

Fig. 4. Pug Mill (Bonnot Co.)

Stone Houses.

In mills using the dry process, the rock goes from the quarry to a stone house. Here it is treated in one of four ways:

1. It is dumped directly into large piles, which are then analyzed, and from this analysis the necessary limestone or clay to be added is calculated. The rock is then loaded on buggies or barrows and wheeled to the crusher after being weighed, where it meets another buggy or barrow loaded with the calculated amount of limestone or clay. The two barrows are then dumped into the crusher together, or one after the other. In some mills

using cement rock, the rock is not weighed before being dumped and the barrows are then merely averaged as weighing so much. The limestone is then averaged also and proportioned somewhat in this manner, two barrows of rock to one barrow of limestone, etc.

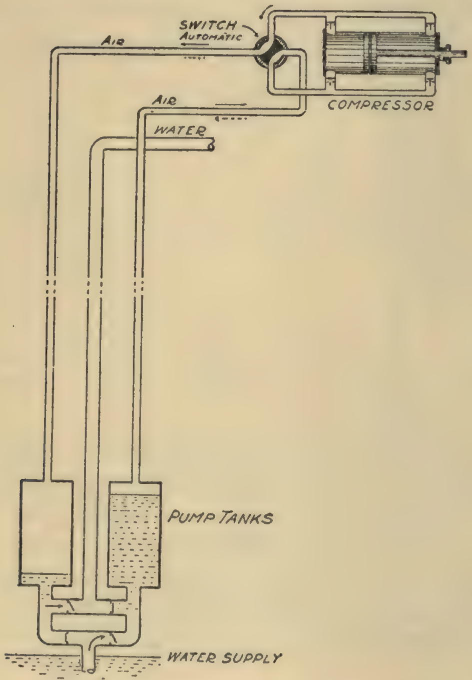

Fig. 5. Harris System of Pumping Marl by Compressed Air.

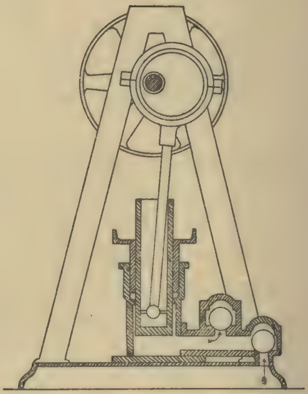

Fig. 6. Ball Valve Slurry or Marl Pump.

2. The rock may be weighed as it comes from the quarry and the proper amount of limestone or clay, as calculated from quarry analysis, added. Part of the cars are then dumped into the crusher and the others are dumped into a pile for night, when it is necessary to wheel from these to the crusher with barrows, etc. At several mills all the cars are dumped into the crusher, part of the stone going to the mill and part of it being stored in bins for the night. The rock is drawn from the bins upon belt conveyors running to the mill.

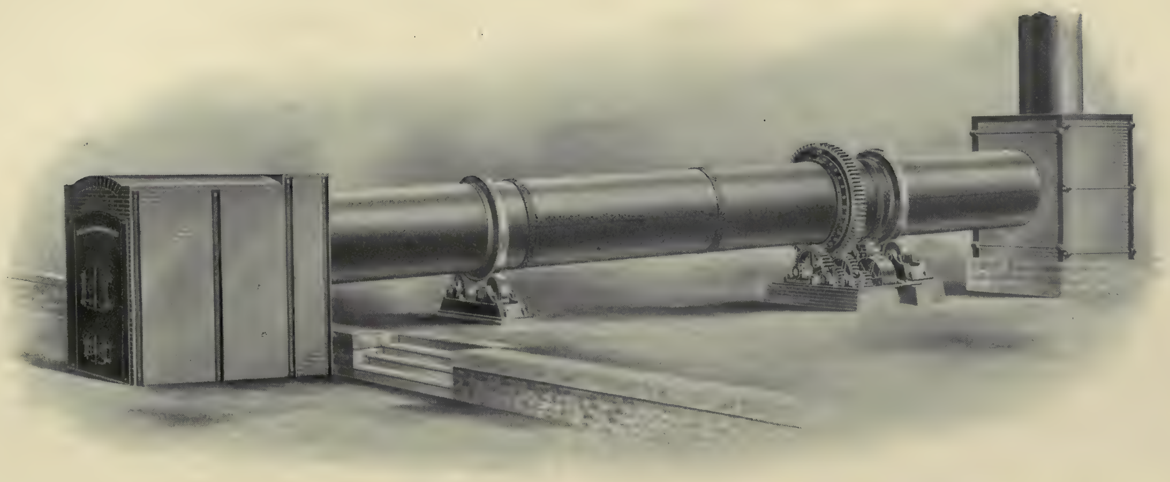

Fig. 7 A. Rotary Dryer.

3. The rock is dumped into the crusher and conveyed into bins, where it remains until the bins are analyzed, when it is drawn out and mixed with a proper amount of crushed limestone or clay held in another bin.

4. A better way than any of the above, is to pass the rock and limestone through the ball mills and grind to a fineness of say 10 to 18-mesh, store in separate bins of 6 or more hours capacity, analyze each bin and then make the mixture of the two accordingly. This is a particularly desirable way, in the case of a clay and limestone mixture, as segregation of the two can not occur in the tube mills as both are finely ground and the mixture of clay and limestone is a homogeneous one. In piling rock either in bins or piles, the coarse pieces will roll down the sides and the fine ones remain in the centre of the pile. In drawing from such a pile, it is a hard matter not to start with fine and wind up with coarse particles if the drawing is done from the centre, or in working in from the edge of the pile, not to start with coarse particles and wind up with fine. As in a cement rock-limestone mix the finer particles are apt to be the soft cement rock and the coarser ones the hard limestone the difficulty of keeping a uniform mix by the methods now in vogue will be understood. In few of the mills of the Lehigh District has any great amount of thought been expended to aid the chemist in making a uniform mix (the usual thing sought being merely economy in handling the rock), and it is to the credit of the chemists of this region, working on such variable material as cement rock, that the Lehigh Valley brands hold the position they do.

The mechanical equipment of the stone house usually consists of the crushers and dryers. The former are usually of the Gates gyratory rock-breaker form, which will be described in the next chapter. The general practice at even the large mills seems to be to use several small crushers in place of one large one. The rock usually falls from the discharge of the crusher into the elevator buckets and is dropped from them into a spout leading into rotary dryers, Fig. 7 A. These are cylindrical in shape, about 4 feet in diameter and 40 feet in length. They are unlined and are usually provided with angle irons bolted to the inside to act as shelves (Fig. 7 B) to carry the rock up and expose it to the hot gases. Some of them have their upper half divided into four compartments (Fig. 7 C) by means of plates in order to expose a greater surface of rock. They are heated by a coal fire at the lower end.

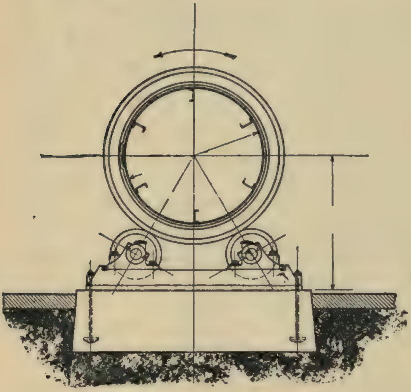

Fig. 7 B. Rotary Dryer, Shelves.

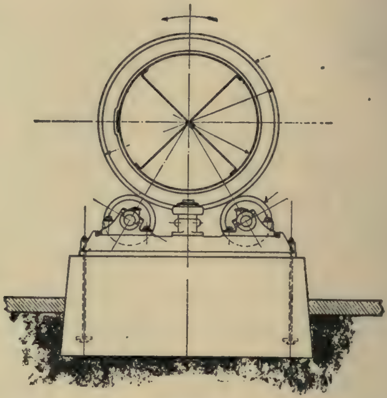

Fig. 7 C. Rotary Dryer Compartments.

They are similar in construction to the rotary kiln described in Chapter VII. One dryer, 40x4 ft., will take care of about 200-250 tons of rock in 24 hours

Wet Process.

The marl is usually received at the mill whether it comes by cars, barge or pipe line in the form of a thin mud. After removing roots, sticks, stones, etc., this slurry is stored in large concrete basins or steel tanks. The clay is usually dried to facilitate the chemical work of obtaining a proper mixture, and disintegrated in edge runner mills or dry pans. From the storage tank the marl is pumped either into a tank of known volume or the hopper of a scale. The clay is elevated to bins above this and mixed as directed by the chemist. From the measuring tank or scales, the mixture is dumped into a "pug" mill and thoroughly mixed. From the pug mill the mass is run into large vats where it is sampled and analyzed. If of correct composition it is passed on for final grinding, if not, the required quantity of marl or clay as the case may be, is added. There should be three or more of these vats so that one may be filling, one analyzed, and the third emptied all at the same time. These vats are provided with stirrers so as to keep the mass in constant agitation to prevent any part of it settling out and also to mix in thoroughly any clay or marl that may be added here to correct the mix. Compressed air is also used for agitating the contents of the slurry tanks in place of the revolving arm with paddles.

Agitators of the propeller form are also used, in which the shaft is horizontal instead of vertical and about which blades are fixed.

As dredged from the deposit the marl contains from 40 to 50 per cent. water, which is usually increased in the pug mills, in order to facilitate pumping it from one part of the mill to another, so that the slurry usually contains from 60 to 65 per cent. of water. Various mechanical means have been proposed for extracting the moisture from the slurry. The following[1] is a list of these:

1. Hydraulic filter presses.
2. Perforated belt passing between rolls which press out the moisture.
3. Large wheels with wide perforated faces between which the material is pressed as it passes through.
4. Steel tank lined with porous tile and air pressure applied, forcing the water through tile, and tank is then drained.

It seems doubtful, however, if any of these mechanical means will succeed because of the fine state of subdivision in which the marl and clay exist in the slurry. At the present, therefore, the only way of getting rid of this excess of water is by evaporation. At one or two plants the attempt has been made to dry the marl in dryers similar to those used for dry materials, such as cement rock, and to use a dry process. The general plan, however, now seems to be to dry the slurry in the upper part of the rotary kiln during burning, making burning and drying one operation.

Examples of Treatment of Raw Material Preparatory to Fine Grinding.

Below will be found short descriptions of the methods employ-

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[1] Soper, Cement and Engineering News, Feb., 1904.

Wet Process Mills.

EGYPTIAN PORTLAND CEMENT CO.—*Raw Materials, Marl and Clay.* Marl is dug up by a dipper dredge and dumped into a stone separator on a scow lashed to the dredge, from the separator it is transferred to barges, which convey it to the shore, where they are unloaded and the marl pumped to the mill by a ball-valve Bonnot slurry pump. At the mill the marl is received in two large tanks which discharge into a pug mill. The clay is unloaded on the floor of the clay house and ground in a dry pan, after which it is screened and elevated to a bin close to the marl bin. The marl and clay are then mixed in the pug mill in proper proportions, passed into a storage tank, ground in emery mills, and then spouted to either of two shallow pits, where it is held for analysis and corrected if necessary. The slurry is then pumped through the tube mills for the final grinding.

BRONSON PORTLAND CEMENT CO.—*Raw Materials, Marl and Clay.* Marl is excavated by a dipper dredge mounted on a scow, which floats in the channel cut by the dipper. The marl is carried to the mill by cars, which dump into pug mills made to act also as stone separators. From these the marl is spouted into concrete storage tanks, where it is analyzed and pumped to the mixing floor. The clay is ground in edge runner mills (or dry pans) and from these elevated to a bin above the mixing floor, where it is added to the marl, in the amount determined by analysis; after which the mixture is thoroughly pugged, the pug mills discharging by gravity into tube mills where the final grinding takes place.

OMEGA PORTLAND CEMENT CO.—*Marl and Clay.* Marl is dredged, the dipper dropping it into buckets on cars, each car carrying two buckets and each bucket of one cubic yard capacity. The cars are hauled to a trestle or trolley, which picks up the buckets and carries them into the wet mill, where they are discharged into a stone separator. From the stone separator the marl passes into vats where, after thorough agitation, it is sampled and analyzed. It is then pumped into three-yard measuring cylinders, the proper amount of clay addeed to it, and the mixture passed through a pug mill to the tube mills for final grinding.

NEWAGO PORTLAND CEMENT CO.—*Raw Materials, Marl and*

Clay. The marl is dredged and lifted to 50-ton cars, which dump it into a bin (or a storage place under a trestle for use in winter). From the bin the marl flows through a bottom valve into a stone separator and enough water is added to make the slurry manageable with a pump. From the separator it passes to three 90-cubic-yard storage bins where it is analyzed. It is then pumped to measuring tanks where the clay is added. The clay after being received at the mill is dried, passed through rolls and into a pug mill where water is added. On passing out of this, it is ground between buhr stones and pumped to the measuring tank to be added to the marl. From the measuring tanks the mixture is fed to a measuring hopper and thence to three 90-cubic-yard tanks where it is analyzed and corrected if necessary. From these vats the slurry passes to the tube mills, where it is finely ground for burning.

CHAPTER VI.

GRINDING THE RAW MATERIAL AND GRINDING MACHINERY.

In the early days of the industry when the plants were small, manufacturing only a few thousand barrels a year each, both the raw rock and the clinker were ground with mill stones, just as natural cement is now, and just as corn is ground in the small water power mills familiar to every one. The first advance upon this was to encase the stones, and as the mills began to work up a home market for their product and to increase their output to meet this demand, they also began to experiment with various forms of fine grinders. As a result of their experiments the Atlas Portland Cement Co. patented the Huntington mill which they still use. In 1889 the American Cement Co. installed a Griffin mill in their plant at Egypt and this mill is still in use there, and in many other large mills throughout the country. Another system of grinding consisting of a ball mill for the coarse grinding and a tube mill for the final pulverization was introduced about this time by the Bonneville Cement Co. in their plant at Siegfried, Pa., and this combination also has come into prominent use in the industry. Recently the Kent mill has been introduced in several Portland cement plants, and its users report favorably upon it.

Edison in his new mammoth plant at Stewartsville, N. J., has installed a system of grinding by rolls. The rock passes in a solid stream through the rolls, undergoing considerable compression as it does so. The crushed material is then dropped in front of revolving fans which blow out the fine particles into large settling chambers. The coarse material is then returned to the rolls, etc.

Crushers.

In the use of any of the above mills upon dry raw materials it is necessary to break up the material to a size of about 2-3 inches in diameter. In order to do this, as has been stated, crushers of the Gates gyratory type are usually employed. This crusher was developed by the Gates Iron Works, Chicago, but is now made and sold by several firms. The jaw or Blake crusher is also used to some extent, though nothing like so generally as the gyratory type. The Gates crusher is sometimes followed by a coffee-mill crusher, particularly where Griffin mills are used for fine grinding. This coffee-mill crusher is described in the section on pulverizing coal in Chapter VII. The Williams mill also used after the Gates crusher and before the tube mill or Griffin mill is also described there.

Below will be found descriptions of the Griffin, three-roll Griffin, Huntington, ball and tube mills, and the Kominuter, and on page 98 will be found a table showing the capacity of these mills and the power required to run them.

Gates Crusher.

Fig. 8 shows a section of a Gates crusher. Referring to this illustration, on the spindle *g*, is mounted the chilled-iron crushing head *c*. The hopper-shaped top shell *h* is lined with concave chilled plates. The crushing is done in the annular space between the chilled surfaces.

The spindle being centrally held in the spider at the top rests at its lower end, passing loosely through an eccentric driven by bevels *b*. The spindle thus receives a gyrating motion and may or may not rotate. Thus, one point in the annular space is wide, while a point opposite is narrow, and the crushing force is obtained on account of the head approaching and receding from the concaves. In the type described the largest motion is at the bottom where the annular space is narrow, and this motion is the throw or stroke. The number of revolutions of the spindle and number of strokes correspond, generally being about 200 per minute. On a crusher having an annular opening at the top, 10 in. × 60 in. circumference, the stroke would generally be about ⅝ inch. These machines work continuously and for this reason are steady in the power required.

As far as oscillating motion goes they are not balanced and therefore give rise to vibration if not on good foundation.

They are used for the very largest capacity. They are well adapted for careless feeding or feeding directly from cars, and the rock can be fed from all directions.

The machines are massive and repairs generally require handling large parts. On account of the sidewise rolling of the head upon the "concaves" this crusher is less liable to choke than the ordinary jaw crusher.

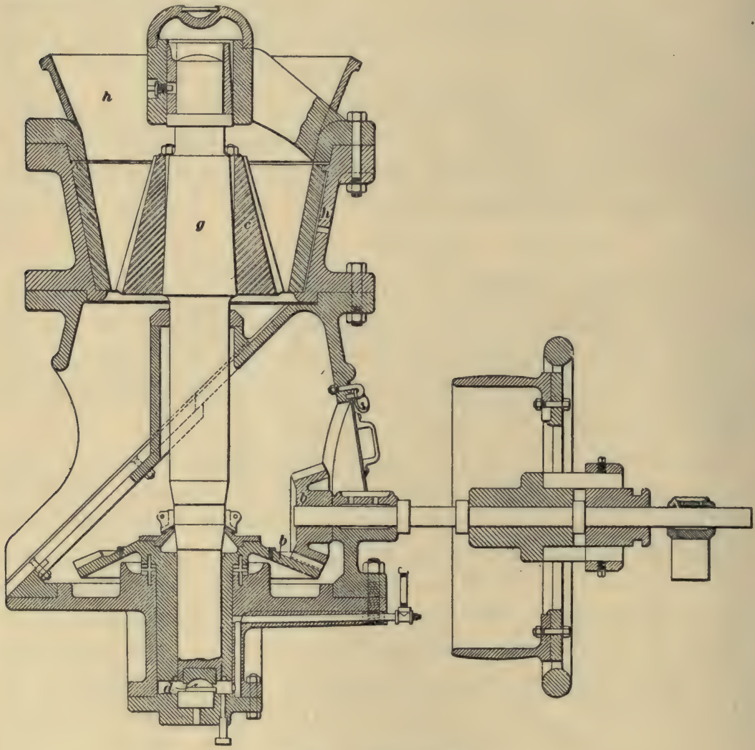

Fig. 8. Gates Crusher.

The power required to operate this crusher upon rocks of moderate hardness is from 1 to 1.2 H. P. per ton of rock crushed per hour.

Blake Crusher.

The Blake crusher is shown in Fig. 9. It consists of the following parts: *f,* the frame; *k,* zinc backing; *c,* still plate or stationary plate; *c,* movable jaw plate; *d,* jutman; *b,* swing jaw or movable jaw; *e,* toggle bearings or seats; *p,* toggles; *t,* front or toggle block; *w,* back or wedge block; side liners or checks, one at each side of mouth; *g,* shaft and eccentric; *h,* bar or swing jaw shaft.

The eccentric shaft pulls up the pitman, straightens out the toggles and this moves the swing jaw while crushing. The angle between the plates requires to be small enough to nip the rock, but large enough to give capacity or a large mouth without excessively long plates. The movement at the bottom or throat is the stroke. The number of effective strokes is the same as the number of revolutions of the pulley, since no crushing is done on the return stroke; the rod *m* pulls the swing jaw back against the toggles during the return stroke. Half the time is occupied, therefore, in storing up energy in the flywheels.

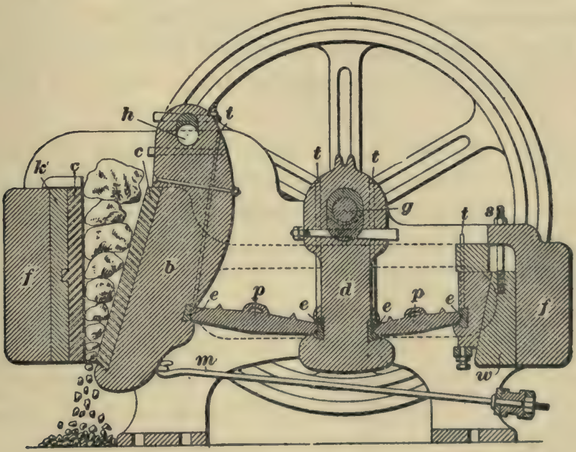

Fig. 9 Blake Crusher.

The Griffin Mill.

The Griffin mill is shown in Fig. 10. Referring to this it will be seen that the power is received by a pulley (17) running horizontally. From this pulley is suspended the shaft (1) by means of a universal joint (9) and to the lower extremity of this shaft is rigidly secured the crushing roll (31), which is thus free to swing in any direction within the case.

A reference to the illustration on the opposite page will show that this case consists of the base, or pan (24), containing the ring, or die (70), against which the roll (31) works, and upon the inner vertical surface of which the pulverizing is done.

In dry pulverizing this pan, or base (24), has a number of openings through it downward, outside of the ring, or die, which lead into a pit, or receptacle, from which it is delivered by a conveyor.

Upon this base is secured the screen frame (44), which is surrounded with a sheet-iron cover (45), (in the wet mill this cover is not used), and to the top of which is fastened a conical shield (25), open at the apex, through which the shaft works.

The cut on page 90 shows the pulverizing roll attached to the lower end of the shaft (1), and just above the roll is the fan (7), which is used in the dry mill, but not in the wet. On the under side of the roll are shown shoes, or plows (5), which are used in both, and varied in shape according to the nature of the work to be done.

The pulley (17) revolves upon the tapered and adjustable bearing (20), which is supported by the frame composed of the standards (23). Two of these standards (23a) are extended above the pulley to carry the arms (22), in which is secured the hollow journal pin (12).

Within the pulley is the universal joint from which the shaft (1) is suspended. This joint is composed of the ball, or sphere (9), with trunnions attached thereto. These trunnions work in half boxes (11) which slide up and down recesses in the pulley-head casting (16).

The joint in the pulley is enclosed by means of the cover (13), thus keeping the working parts away from all dust and grit.

The lubricating oil is supplied for all parts needing it through the hollow pin (12).

The roll is revolved within the die in the same direction that the shaft is driven, but when coming in contact with the die it travels around the die in the opposite direction from that in which the roll is revolving with the shaft, thus giving the mill two direct actions on the material to be ground. There is a pressure by centrifugal force of 6,000 pounds brought to bear on the material being pulverized between the roll and die, the united actions being very effective in their combination.

When a quantity of the material to be reduced has been fed into the mill, sufficient to fill the pan as high as the shoes, or plows, on the lower side of the roll, they work in it, stir it up, and throw it against the ring, so that it is acted upon by the roll; and when fairly in operation the whole body of loose material whirls around rapidly within the pan, and, being brought between the roll and die, is crushed, and all that is sufficiently fine passes at once through the screen above the die, the coarser portion falling down to be acted upon again.

The universal joint, by which the shaft is connected with the pulley, allows perfect freedom of movement to the roll, so that it can safely pass over pieces of iron, steel, etc., such as are usually found in all material to be pulverized, without damage to the mill.

The fan attached to the shaft above the roll draws air in at the top of the cone, forcing it through the screens and out into the discharge, thus effectually keeping all dust within the mill.

In working dry the screen which surrounds the pulverizing chamber is of much coarser mesh than the delivered product; for instance, a 16 mesh screen delivers a product over 90 per cent. of which will pass a 100-mesh screen. There is, in consequence, no clogging by reason of having to use fine mesh screens in order to secure fine products.

A Griffin mill of the size usually installed in Portland cement mills will grind from 1½ to 3 tons of rock per hour, the amount varying with the hardness of the rock and the condition in which the mill is kept. In doing this work it will consume from 25 to 28 horse power. The cost of keeping these mills in repairs is from 1 to 1½ cents per barrel ground.

Three Roll Griffin Mill.

This is a new mill recently brought out by the manufacturers of the Griffin mill, which is somewhat similar in principle to the single roll Griffin mill. It is shown in Fig. 11, and as its name implies it has three rolls in place of one. It is provided with screens, fans and ploughs which perform the same work as in the old style Griffin mill. These mills have been given a thorough trial on grinding raw material, but so far have been only used

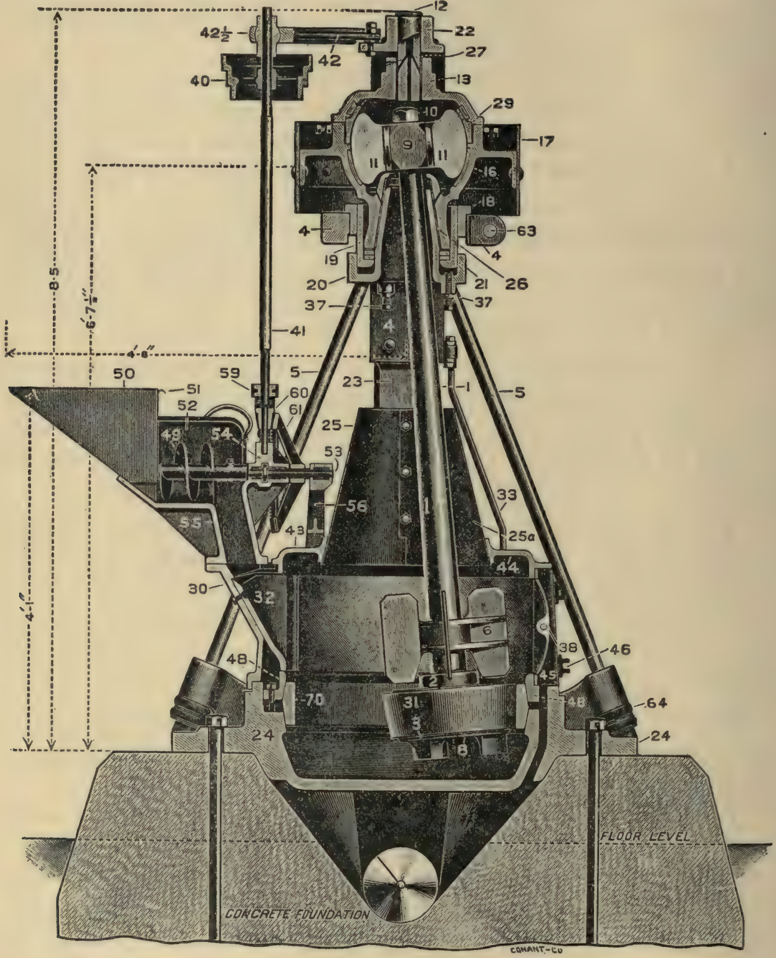

Fig. 10. The Griffin Mill.

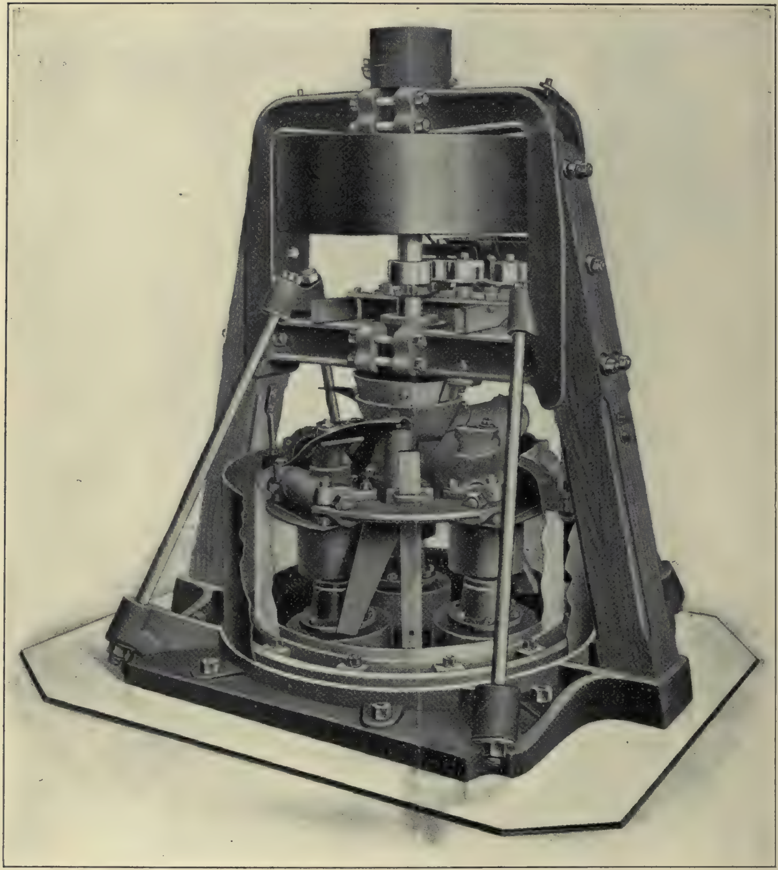

Fig. 11. Three Roll Griffin Mill.

experimentally for grinding clinker. One of the newer mills in the Lehigh District has its entire raw side equipped with these mills and reports from this plant credit them with doing remarkably well. The three roll mill requires 40-horse-power to run and will grind 5 to 6 tons of cement rock- limestone mixture per hour to a fineness of 96% through a 100-mesh screen. The new mill is said to be not only more efficient than the single roll Griffin mill, but to also require less repairs, and consequently to cost less to keep in order.

Huntington Mill.

The Huntington mill is another mill of the impact or percussion type and is somewhat similar to the former in construction, so far as the writer knows it is used only by the Atlas Portland Cement Co., Northampton, Pa.

The Huntington mill, Fig. 12, has shells freely suspended on spindles from a revolving spider. The revolution causes the shells to swing out and crush against the edge of the die ring. The machine generally is a great consumer of repairs.

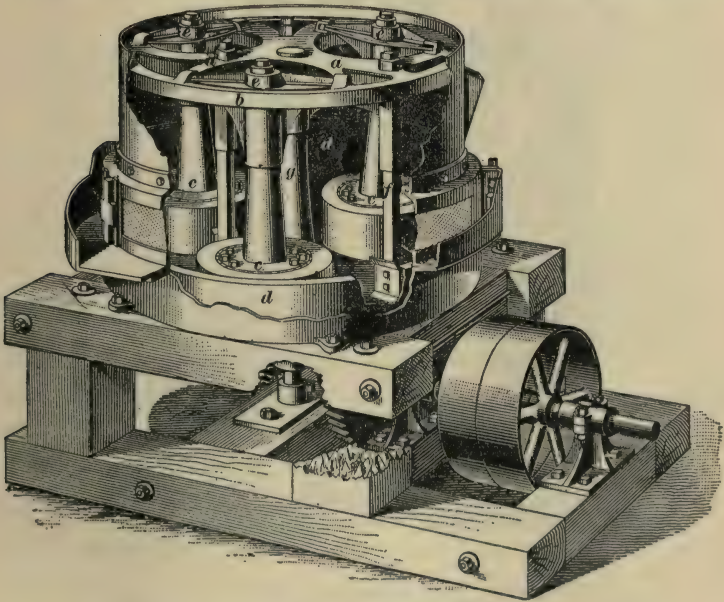

Fig. 12. Huntington Mill.

The Ball Mill.

The ball mill is of European origin and was used for grinding Portland cement in Germany before its introduction into this country. It is usually used in connection with the tube mill to prepare the material for the latter, the ball mill reducing it to a coarse grit and the tube mill completing the operation.

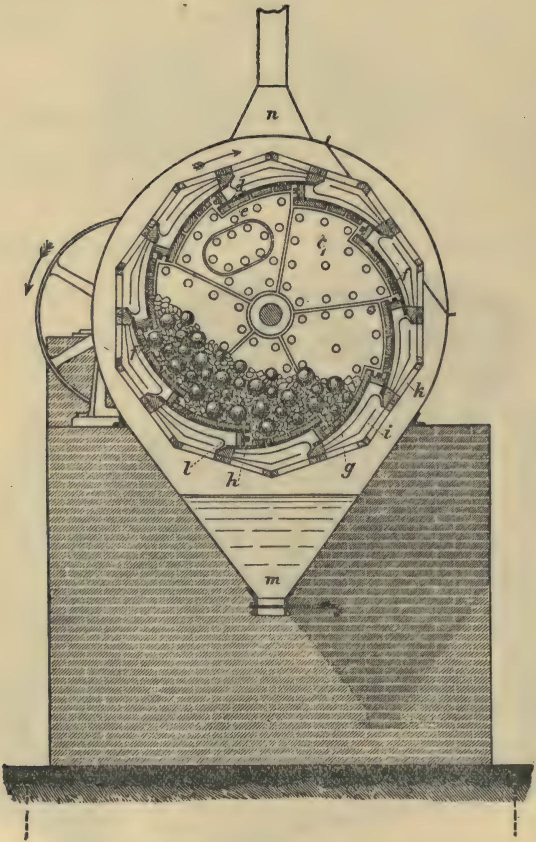

Fig. 13. Ball Mill, Section Showing Grinding Plates and Sieves.

Figs. 13 and 14 show the construction of a ball mill. It consists of a drum filled with steel balls. The drum is lined first with steel plates, *(d)* which lap one over the other to form steps. As the drum revolves, the balls drop over the steps pounding the material to pieces. The partially ground material then drops through holes in the plates on to perforated steel screens *(g)* bolted around

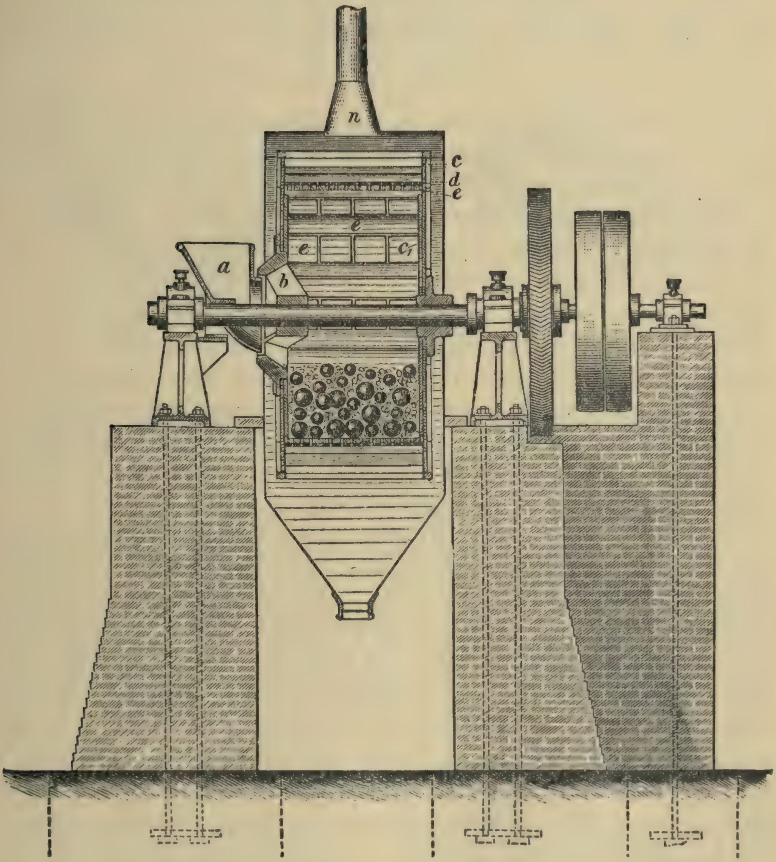

Fig. 14. Ball Mill, Section through the Shaft.

the entire circumference of the drum. These screens take out the very coarse particles and return them to the inside of the drum. The finer ones drop on another set of screens *(l)* made of woven wire cloth, and these separate the fully ground material from the coarse and return the latter back to the mill.

The fully ground material falls into the dust proof casing, which entirely surrounds the mill, and then down to the conveyor running underneath the latter.

The ends of the drum are formed by circular plates. In the Gates and Krupp forms of this mill and also in the smaller size of the Smidth mill these plates have rigidly attached to their centres, hubs which are mounted on to a heavy shaft which revolves in dust-proof bearings. One of the hubs is provided with openings through which the material to be ground is fed. In the large size Smidth mills the shaft is omitted and the hub rests on roller bearings giving a full circular opening which will admit of the passage of lumps 10 inches in diameter into the mill. The feeding device of the Smidth mills consists of a circular revolving table provided with a scraper. The material to be ground is brought down upon the table by a spout which stops short a few inches from the former. As the table revolves the material flows out of the spout upon it and as it comes around to the scraper is brushed off into the hopper of the mill. The feed can be regulated by adjusting the scraper so as to brush off a greater surface of the table. The Gates ball mill has a swinging feeder.

The size of the product of the ball mill is regulated entirely by the fineness of the finishing screens. Those on mills intended to grind raw material are usually 16 to 18 mesh and those on mills for clinker from 18-20 mesh. It is generally economy to so balance the screens as to get the most out of the tube-mill, however, since the ball mill requires much less power than the tube-mill and consequently up to a certain point should be made to do all the work it will. The screens of the ball mill are apt to leak occasionally, both from wear and also from the dropping out of a rivet or bolt. A good check upon this is to run sieve tests of the product upon a No. 20 sieve once or twice a day and any abnormal weight of residue should be followed by an examination of the screens for leaks. It is necessary to brush the screens off occasionally with a wire brush as they clog with use.

A ball mill usually requires from 30 to 40 horse power and turns out from 4 to 6 tons of raw material per hour. The balls run in sizes from 3 to 5 inches in diameter and the charge of balls for a mill of the above size weighs usually about a ton and a half.

The Kominuter.

A modification of the ball mill which has been introduced in the last three years by Messrs. F. L. Smidth & Co. is the Kominuter. This form of mill is intended to do the work of the ball mill and has about double the capacity of the latter. It consists, Fig. 15, of a drum of about the same diameter as a ball mill but of about twice the length of the latter, suspended on a shaft supported by bearings. The kominuter is lined just as a ball mill is with wrought iron or steel grinding plates arranged to lap and form steps. The drum is surrounded by a coarse screen tilting slightly towards the feed end, and outside of this screen, yet another one of wire cloth. The material enters through an opening beside the shaft and is pounded to pieces by the balls. It does not fall out through the screens, however, at once, but travels through the full length of the drum and passes through openings at the opposite end, on to the first coarse screen, or perforated plate. The particles too large to pass through this are returned automatically to the interior of the mill by means of buckets and S shaped pipes. The material passing the inside screen is caught upon the outside one of wire cloth and separated further here, the coarse material being returned to the mill as before.

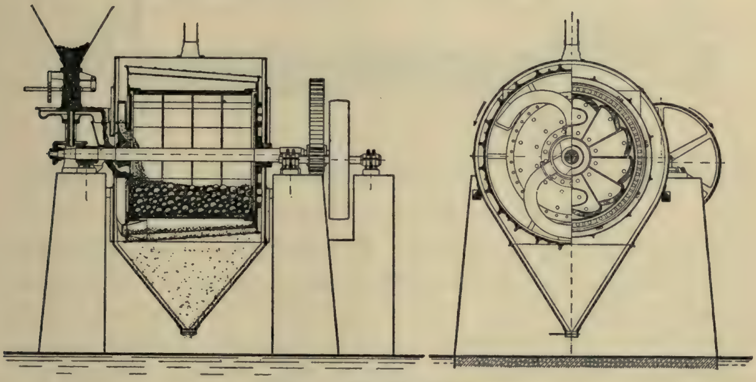

Fig. 15. The Kominuter.

The Tube Mill.

The tube mill, Fig. 16, consists of a cylinder, 20 to 22 feet long, and from 60 to 66 inches in diameter, filled with flint balls. This cylinder is lined with some hard substance such as armor plate, chilled steel, quartz, or trap-rock and revolves at a speed of from 25 to 27 revolutions per minute. The material is fed in through a hollow shaft and leaves either in the same manner at the opposite end or else through a grating at the perimeter of the end. In the Smidth tube mill the latter course is pursued, and in the Gates and Krupp mills the former plan is followed. The Krupp mill is also divided into compartments forcing the material to travel in a zig-zag motion through the mill. The other two types are without compartments. The flint pebbles are generally imported from Europe and wear at the rate of about one pound to thirty barrels of cement. Steel balls are sometimes used in tube mills grinding wet materials. The material is usually fed into the tube mill by means of a screw conveyor operated by a step-pulley which permits the cutting down of the feed, or by a roller feed with movable gate, or by a shaker feed, any of which can be adjusted to regulate the amount of material going into the mill. A tube mill, 5½x20 feet, usually requires 80 horse-power to run and about double that quantity momentarily in starting. It should turn out about 12 to 16 barrels of clinker per hour

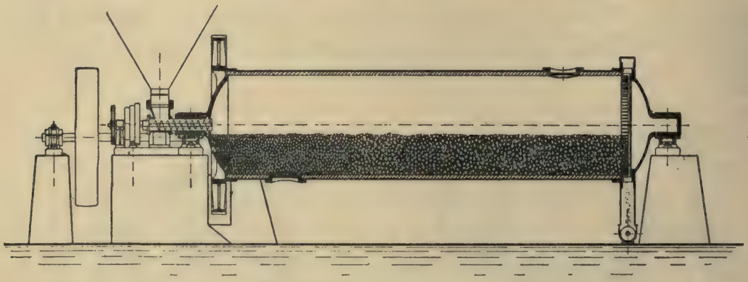

Fig. 16. Smidth Tube Mill.

In the dry process it is usual to grind both the raw material and the clinker in the same type of grinder, though at some mills the raw materials are ground in ball and tube mills and the clinker in Griffin mills. In the wet process the tube mill is nearly always used to reduce the slurry to the necessary fineness, but either ball and tube or Griffin mills can grind the clinker. It is necessary usually to break up the rock with rolls or some other form of crusher before feeding it to Griffin mills. The proposition has been made to do this preparatory work with kominuters. When the wet process is used it is usual to break up the clay with an edge runner mill or dry pan which also serves as a mixer.

It consists of a cast iron pan, in which heavy iron rollers revolve, the clay being crushed between the bottom of the pan and the rollers.

Capacity of Various Grinders.

Below will be found a table (XVII) giving the capacity of the various machines used for crushing and grinding the raw materials and clinker in a cement mill. It is compiled from results obtained in actual practice and the output of the various machines is the average for long periods of time and includes shut-down for ordinary repairs, etc. For instance, when the capacity of a No. 6 Gates crusher is given as 30 to 40 tons per hour it means that this size crusher will crush 300 tons day in and day out of ten hours, and not just 30 tons for a test run of an hour. Similarly when the capacity of a No. 7 ball mill is given at 12 barrels an hour it means that three of them will safely take care of the clinker end of a four-kiln dry process plant, allowing for shut-downs to clean and renew screens, put in new plates, etc. In each case the lower figure in the table is the safe one to assume as the least capacity of the mill in question when properly handled. The fineness of the output is an important item in determining the output of a mill. In one instance which the writer recently observed, a tube mill ground cement on an average 12 barrels an hour to a fineness of 97% through a No. 100 sieve, and on increasing the feed 15 barrels an hour to a fineness of 92% passing a No. 200 sieve, or an increase of 3 barrels an hour, or 25% more for a decrease of 5% in fineness. In making comparisons between two forms of grinders, therefore, it is necessary that the fineness of the product produced by each should be the same, not only when tested by the No. 100 sieve but also by the No. 200, as a difference of 2% in fineness may easily represent a difference of 10% in output.

TABLE XVII.—GIVING CAPACITY, ETC., OF CRUSHERS AND MILLS USED IN GRINDING RAW MATERIALS AND CLINKER.

Type of Mill.	Size.	Charge of Balls. Lbs.	Horse-power Required to Operate.[1] H. P.	Output per Hour.			
				On Hard Limestone. Tons.	On Cement Rock. Tons.	On Marl and Clay. Tons.	On Clinker. Barrels.
Gates Gyratory Crusher.[2]	No. 5 D	......	25 to 40	20 to 30	25 to 35	......	......
	No. 6 D	......	30 to 60	30 to 40	30 to 50	......	......
Ball Mill.[3]	No. 7	3000	30 to 40	3 to 5	4 to 6	......	12 to 16
	No. 8	4500	40 to 50	4 to 7	5 to 8	......	18 to 25
Tube Mill.[4]	5′x22′	......	70 to 80	3 to 4	4 to 6	8 to 12	12 to 16
	5′6″x20′	......	80 to 90	4 to 6	5 to 8	10 to 15	16 to 20
Griffin Mill.[5]	30″	.....	23 to 28	1½ to 2	2 to 3	......	5 to 8
Three Roll Griffin Mill.[5]	......	......	40	......	4 to 6	......	......
Kominuter.[3]	No. 66	6600	40 to 45	5 to 7	6 to 8	......	30 to 35
Kent Mill.[6]	......	......	25 to 35	......	.....	......	10 to 12

Degree of Fineness.

The degree of fineness to which the raw material should be ground depends largely upon conditions. It may be said as a general rule that it should never be ground coarser than 90 per cent. through a 100-mesh sieve and that in most cases 95 to 98 per cent. is required to produce a sound cement. Fine grinding will also lessen the quantity of coal required for burning because the more intimate mixture of the lime with the silica and the alumina promotes a more rapid combination of these elements, as sintering only takes place between surfaces, and the more minute the particles are, the greater surface will be exposed. For a similar reason if the raw material is too coarsely ground the lime can not get at the silica and alumina to combine with them. The fineness of the raw material should be tested at least once a

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[1] About double this power is required momentarily in starting the mills.

[2] Product passing a 1 inch screen.

[3] Fed with product of crusher or clinker as it comes from coolers and provided with 16-mesh screens of No. 23 wire.

[4] Fed with product of ball mills. Finished material 95% through a No. 100 sieve.

[5] Fed with clinker or rock crushed to one-half inch. Finished material 95% through a No. 100 sieve.

[6] Fed with clinker from coolers and finished product to be 95% through a No. 100 test sieve.

day and, if possible, two or three times a day in order to have a check upon the work of the mills and to keep them up to standard. The raw material can be tested on the 100-mesh sieve by the method for fineness outlined in the chapter on "Physical Testing."

Conveyors.

The material is usually conveyed from one part of the mill to another by mechanical means. The product of the Gates crusher is carried to the ball mill bins or the rolls on belt conveyors or scraper conveyors, and the fine material from the ball mills and the tube mills is conveyed by means of screw conveyors. The elevating is done by bucket elevators of the link belt form. Slurry and marl are pumped, using either the compressed air system mentioned before or a plunger pump of special design for the work. Dry material is stored in steel bins at every stage of the process in order to have a constant supply for each unit of the grinding system, and marl and slurry are stored in concrete vats or steel tanks and kept in constant motion to prevent the heavier and sandy portions from settling out.

CHAPTER VII.

KILNS AND BURNING.

Shaft Kiln.

The first Portland cement made both in Europe and America was burned in upright or dome kilns, in which the raw material is moulded into bricks and charged alternately with layers of coke. The kiln is unloaded at the bottom and, after the clinker is drawn, it is carefully gone over by men or boys and the over burned and underburned sorted out and rejected. The properly burned clinker only is ground. These kilns are similar to those used for burning lime, and their form is shown in Fig. 17. From their shape they are also called "bottle" kilns. They are intermittent in action, that is they must be freshly charged for each burning. On this account there is considerable loss due to the necessity of heating up the kiln for each burning. Saylor burned his first Portland cement in these kilns and the first mills in the Lehigh Valley all used this form of kiln. In Europe where the bricks were made

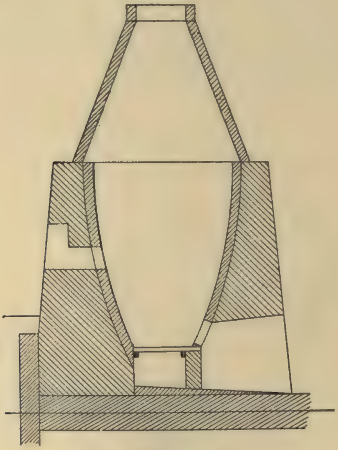

Fig. 17. Dome Kiln.

from the more or less plastic mixture of chalk and clay no difficulty was experienced in forming the bricks; in this country, however, the fine crystalline cement rock did not have sufficient binding power of itself to make bricks of the strength to withstand the weight of the charge above them in the kilns, and it was found necessary to incorporate with it a small proportion of Portland cement, to give it binding power. At the American Cement Co.'s plant at Egypt, Pa., the fine powder was mixed with liquid hydrocarbons to form a stiff paste, which was moulded by compression into bricks. This process saved drying the bricks and promised well, when the introduction of water gas raised the price of coal tar, and necessitated the abandonment of the scheme.

The first efforts made to improve the "bottle" kiln were naturally to use the waste heat in the products of combustion coming off at the mouth of the kiln for drying the bricks. Fig. 18 shows the form of kiln invented in 1872, by Mr. I. C. Johnston, of Greenhithe, England, for this purpose. *A* is the kiln and *B* is the drying chamber. The kiln is charged with the bricks which have been dried by the heat of the previous burn. The wet bricks for the next charge are placed at the same time, in the tunnel-shaped flue and the hot gases from the kiln pass over and around them, and dry them thoroughly. These kilns are, of course, more satisfactory than the ordinary "bottle" kiln, but they still waste much heat. The hot clinker, of course, carries off a great deal, and the cooling off of the kiln itself causes additional waste. These kilns were installed in the original mill of the Western Portland Ce-

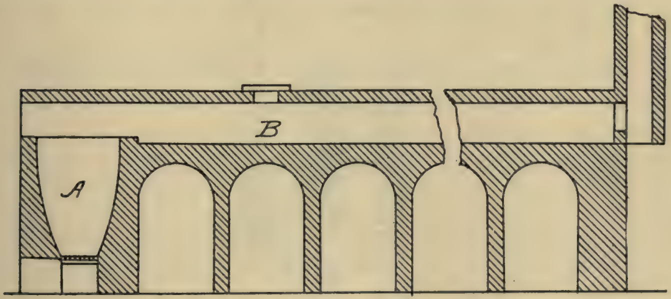

Fig. 18. Johnston Kiln.

ment Co., Yankton, S. D. The time lost in drawing the clinker, charging the kiln and heating it up, as well as the heat losses, led to the design of continuous kilns, in which the charging is carried on continuously at the top, and the clinker is drawn off from time to time at the bottom. Among the best known of these kilns are the Hoffmann ring kiln, the Schœfer and the Deitsch kilns, the latter two are modifications of the *etagen-ofen* or kiln of several stories. These kilns are all economical of fuel, but all require the material to be made into bricks for burning and the clinker to be sorted.

The Hoffmann kiln is shown in Fig. 19. It consists of a ring of chambers, built around a large central chimney. Each chamber is connected with the chimney by a flue

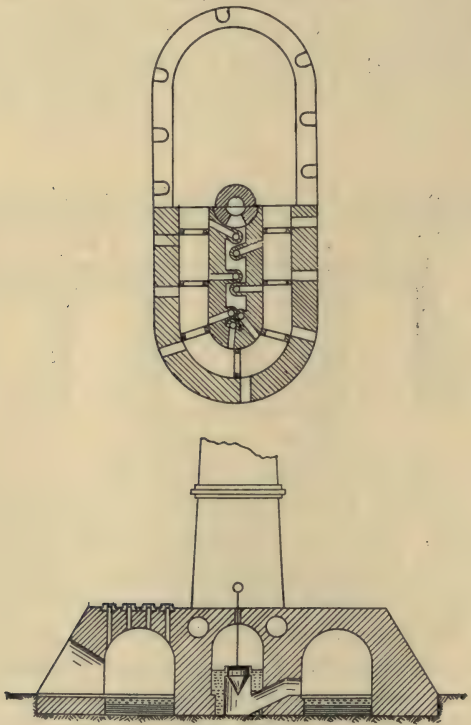

Fig. 19. Hoffmann Ring Kiln.

and has a door opening outwards. The chambers are also all connected with each other. The bricks are piled up in the chambers, just as they are in a brick kiln, so that the products of combustion can pass around them and between them. The oven is operated as follows: When a chamber is loaded, it is shut off from the succeeding one, which is empty, by a sheet iron door, and connected with the preceding one. The flue leading into the chimney is also opened and the corresponding flue in the preceding chamber is closed. By this means, the waste heat from the compartment, whose contents is being burnt, is passed forward, around the ring of compartments, to the one just charged, and thence through the flue and up the chimney. By this means the contents of the chambers are gradually heated up, the bricks are dried in the chambers near the flue and then become hotter and hotter as the chamber of combustion is brought nearer. The air for burning is passed through the chambers in which burning is completed and is thereby itself heated and the clinker cooled. It is usual to load one compartment each day, and of course, to draw one. The fuel for burning is not loaded in with the bricks, but is fed in from openings at the top of the kiln during burning. The Hoffmann kiln is very economical of fuel, but requires much skilled labor if it is to be operated successfully. The bricks have to be carefully piled and the charging requires skilled hands. This kiln is much in use in Germany, but so far as the writer knows, has never been used in this country for burning Portland cement.

The Dietsch kiln is shown in Fig. 20. It was patented in 1884. It consists of a cooling chamber *H*, a burning chamber *F* and a heating chamber *C*. The kilns are usually built in pairs, back to back. The kiln is loaded through the door *A*, and as clinker is drawn out at the bottom, the dry slurry drops down into the heating chamber where it is gradually brought up to a high temperature. From the heating chamber it is raked over into the combustion chamber, by introducing a tool in the door *E*, and fuel for the burning is mixed with it through the same door. The burning is completed in *F*. The cold air for combustion is heated by passing through the red hot clinker in *H*, cooling the latter. Eyes

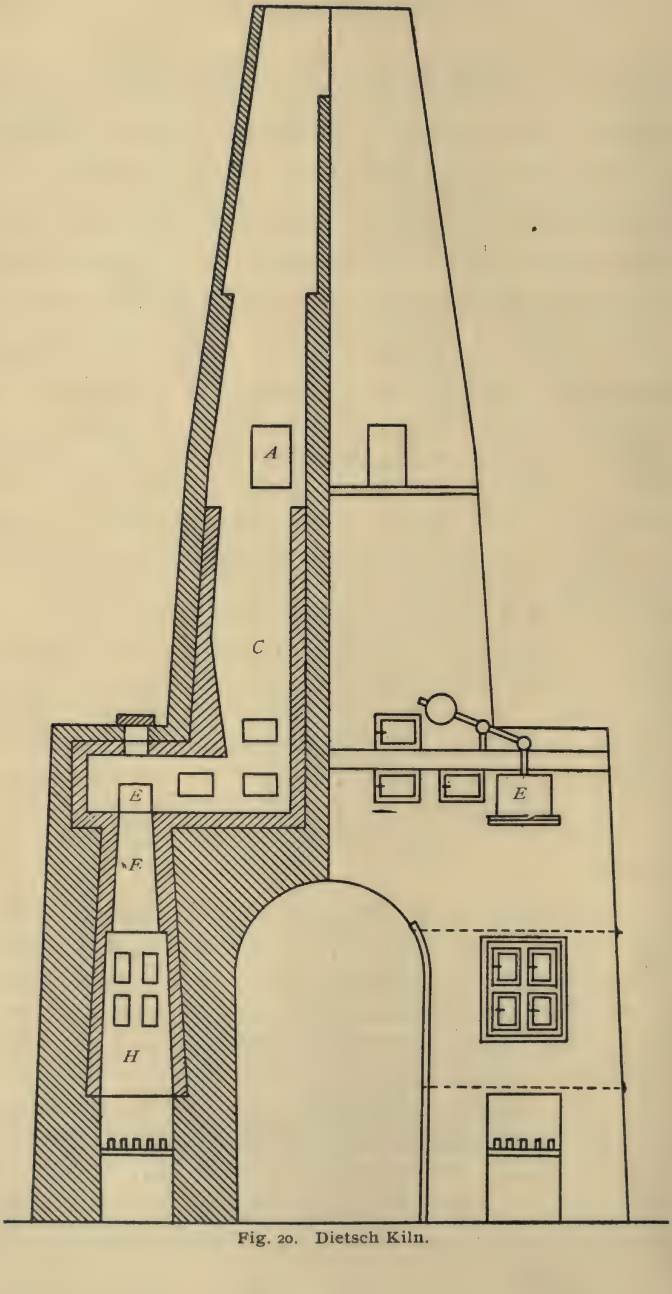

Fig. 20. Dietsch Kiln.

are placed at the lower levels of the combustion chamber, through which bars may be inserted to detach the sintered mass should it hang up, due to overburning. The Deitsch kiln is also economical of fuel, but does not require the slurry to be made into bricks. Several were introduced into this country in the early days of the industry, one being built for the Buckeye Portland Cement Co., of Bellefontaine, O. A modification of the Deitsch kiln perfected in Denmark and known as the Schoefer kiln, was introduced into several of the earlier cement mills and was used, I believe, by

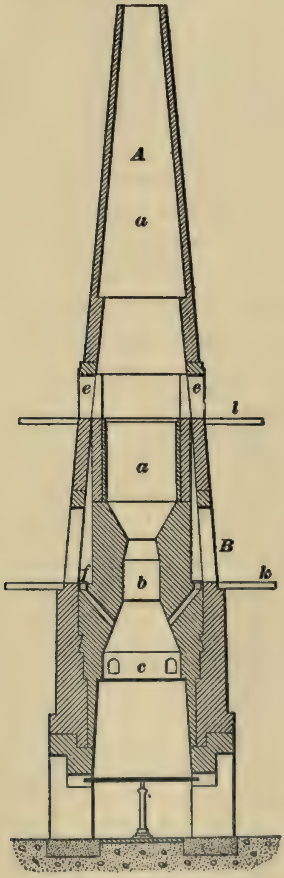

Fig. 21. Schoefer Kiln.

the Glens Falls Portland Cement Co., Glens Falls, N. Y., exclusively, and also by the Coplay Cement Co., at one of their mills, at Coplay, Pa., where eleven were once in use. The Schoefer kiln is shown in Fig. 21. It operates upon the same principle as the Deitsch kiln and consists of a long vertical flue, the upper part of which serves as a preheating chamber, the middle narrow part as a combustion chamber and the lower section to heat the draft.

With all of these kilns the product has to be sorted and the underburned portions picked out and reburned. They are also troubled with dusting clinker:—that is, clinker which falls to a powder on cooling. This fault is supposed to be caused by burning with a reducing flame due to the formation of carbon monoxide from either incomplete combustion or decomposition of the carbon dioxide by the red hot coke. These shaft kilns require only about 45 pounds of coal per barrel, but the labor cost connected with them is two or three times as great as the fuel cost. The shaft kilns themselves cost about as much as a rotary kiln, but only turn out about half as much clinker.

The Rotary Kiln.

The kilns above described are still used largely in Germany; in France and Belgium, the Candlot and Bauchere kilns are used, and in England the Johnston kiln is much employed. In this country the cost of moulding the raw material into bricks was considerable, and the sorting of the clinker, made necessary by the uneven burning in these kilns, further increased the cost of manufacture. Abroad where labor is much cheaper than it is in this country, these operations could be carried on successfully, so that European cements could be brought to this country and sold in competition with American cements at a good profit. Their reputations were established and they could successfully hold their market against the home manufacturers, who could not afford to cut the price of their cement owing to the high cost of manufacturing due to the expensive labor item, so that all the early manufacturers were seeking a cheaper method of burning, one that would do away with the employment of so much hand labor and allow them to compete successfully with their foreign rivals. This led them to experiment with the rotary kiln which had been invented in 1873 by F. Ransom, an English engineer, but which had never been successfully used in England. In this country the first plant to attempt its use was a small plant in Oregon[1], in 1887, but the attempt proved a failure and the plant itself was shut down, owing to litigation among its stockholders. About the same time the Atlas Portland Cement Co. began to experiment with Ransom's kiln at first at East Kingston, New York, on wet materials and later with success upon the cement rock of the Lehigh District at Northampton. At first they met with many difficulties, and it was only after much experimenting, that they succeeded in making it work successfully. They found that owing to the shorter time during which the material underwent calcination, it was necessary to grind it much finer than had been necessary with the old bottle shaped kilns. They also found it necessary to carry the lime a little higher, in their raw material than had been done before, and to moisten it slightly with water. It is undoubtedly true that to the Atlas Portland Cement Co. and to its officials, Navarro, Giron, Seaman and Hurry, the credit of the commercial development of the rotary kiln is due. In Ransom's original patent he proposed to heat the kiln by producer gas, but its development in this country was made possible, by the use of crude oil, as a successful method of burning powdered coal had not been perfected at that time. At first these kilns were only 40 feet long, but it was soon found more economical to lengthen them, 60 feet being now the usual length.

The rotary kiln in its usual form consists of a cylinder, 6 feet in diameter by 60 feet long, made of steel sheets from ½ to $^9/_{16}$ inches in thickness, lined with fire brick. The steel sheets are held together with single strap butt joints, as these joints resist expansion strains due to heating better than lap joints. This cylinder is supported at a very slight angle from the horizontal on two tires made of rolled steel, and having a 6-inch face and a thickness of at least 4 inches. These tires are not fastened directly to the kiln, but are held 4 to 6 inches from the latter by an arrangement of blocks and plates. They run each on four heavy

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[1] Mineral Resources, U. S. Geol. Survey, 1887, p. 530.

friction rollers usually mounted in pairs on a rocker and made of cast steel. The kiln is driven by a girth gear situated usually near its middle, and a train of gears, actuated either by a line shaft or a motor. The upper end of the kiln projects into a brick flue which is surmounted by a steel stack. The flue is provided with a door at the bottom to take out the dust which accumulates there. Dry material is fed into the kiln by means of a water-jacketed screw conveyor running from the kiln bins, which are situated usually just back of the flue, through the latter, far enough into the kiln to prevent the materials falling into the flue when the kiln revolves. The feeding device is usually attached to the driving gear of the kiln, so that when the latter stops the feed is shut off. When slurry is used, this is pumped into the kiln from a vat below, by either a plunger pump or compressed air. In some instances, it is pumped against the pressure of a standpipe, to insure a constant feed. The lower end of the kiln is closed by a hood into which the kiln projects. Some times this hood is made stationary with movable fire brick doors, but oftener it is mounted on a movable carriage. The front wall of the hood is provided with two holes, one for the entrance and support of the burning apparatus, and the other for observing the operation of the kiln and for inserting bars to break up the rings formed and repair the lining. The lower part of the hood is left partly open, and through this the clinker falls. Air for combustion also enters here. Figs. 22 and 23 show as well as can be done in a small illustration of such a long object the construction of the completed kiln.

The usual diameter of a 60-foot rotary kiln unlined is from 6 to 7 feet. Most of them are made the same diameter throughout, though some of them are made, say 6 feet 6 inches in diameter for the first 30 feet and then taper through 10 feet to a diameter of 5 feet 6 inches for the remaining 20 feet; others taper for the last 10 or 15 feet before entering the stack. This latter plan has the effect of a damper, crowding the heat more to the front of the kiln. It probably lessens the output somewhat, since the choking cuts down the amount of coal that can be burned, but it probably

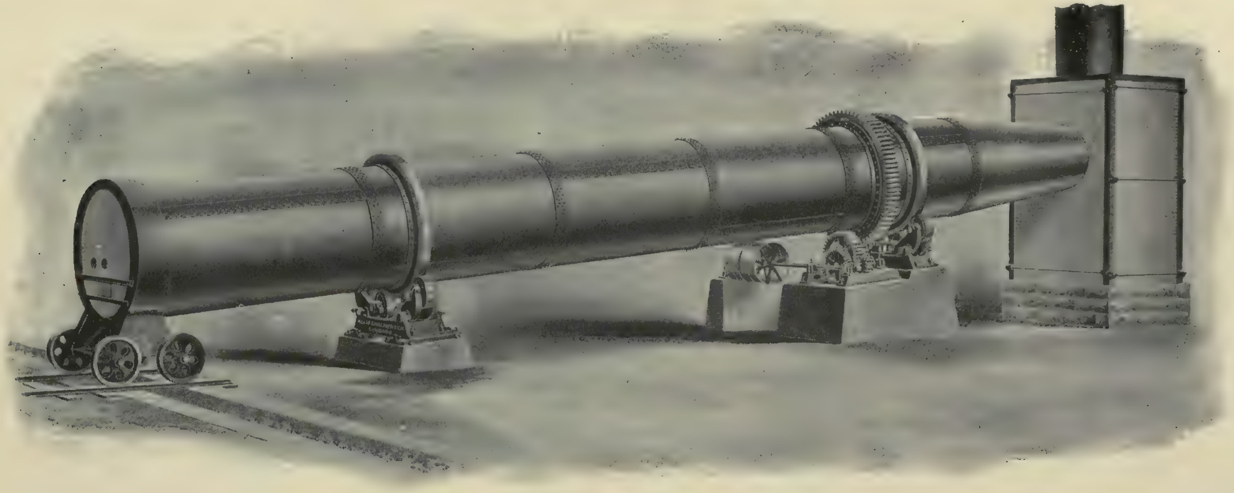

Fig. 22. Rotary Kiln.

also adds something to the economy of the process. Some kilns are made to bear on three tires, but the usual plan for a 60-foot kiln is but two tires.

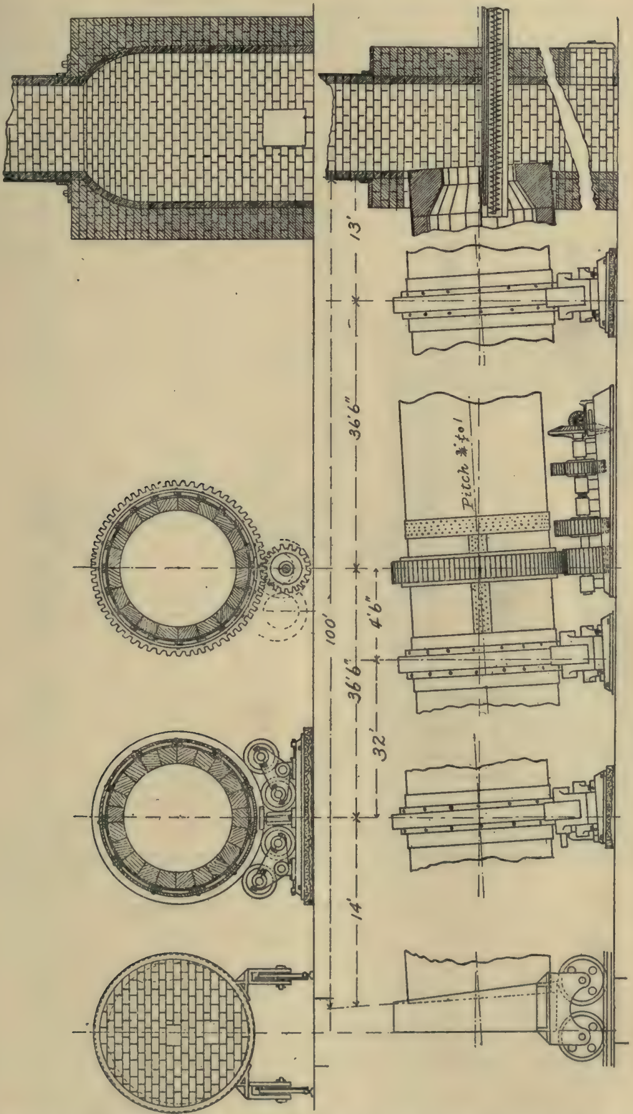

Fig. 23. Detail Construction of a 100-foot Rotary Kiln.

Fig. 24 shows an arrangement designed by the Allis-Chalmers Co. for feeding the material into the kiln by means of a water-jacketed conveyor. It is also possible by moving the stack to one side or behind the flue to spout the material into the kiln through an asbestos-covered spout.

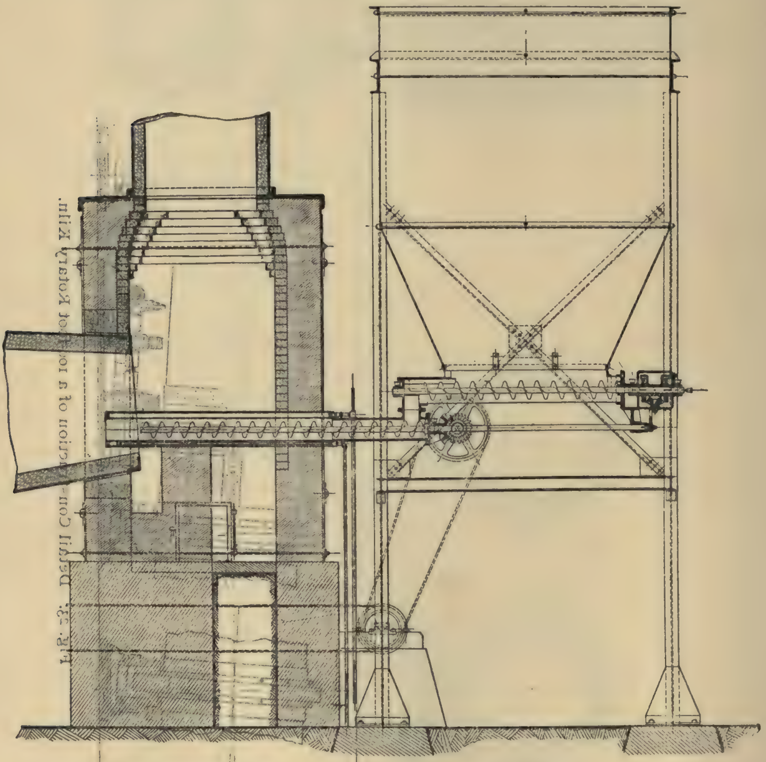

Fig. 24. Stock Bins and Water Jacketed Conveyor for Feeding Raw Material into the Kiln.

The kilns are rotated at different mills at different speeds, varying from one turn in one-half a minute to one turn in three. The average, however, is from a turn in a minute and a half to one in two minutes. Usually the speed can be regulated by some arrangement of an automatic speeder, such as the Reeves, the Mosser speeder or, where run from separate motors, by a controller. In some mills all the kilns are on one shaft and consequently of fixed speed. There are some points in favor of each. Where the speed can be regulated by the burner, he has better control of the burning, but there is sometimes a tendency on his part, where the foreman is lax, to cut down the speed and consequently the capacity of the kiln in order to make his own work easier. Where there is a likelihood of the mix not being regular, speeders should always be put in, as it is easier to control the burning of such material by the kiln speed than by the coal feel. With fixed speed, the kilns are arranged with some sort of jaw clutch, so they can be cut out for patching, relining, etc. It is also necessary occasionally to shut them down for "heat" if the mixture burns hard, or the raw material is fed into the kiln irregularly, causing it to become overloaded. As we have said, the raw material fed into the kiln should be controlled by its speed and be shut off when the kiln stops. A great deal has been said about the proper speed for a kiln to revolve, no two authorities agreeing, and the writer has come to the conclusion from personal

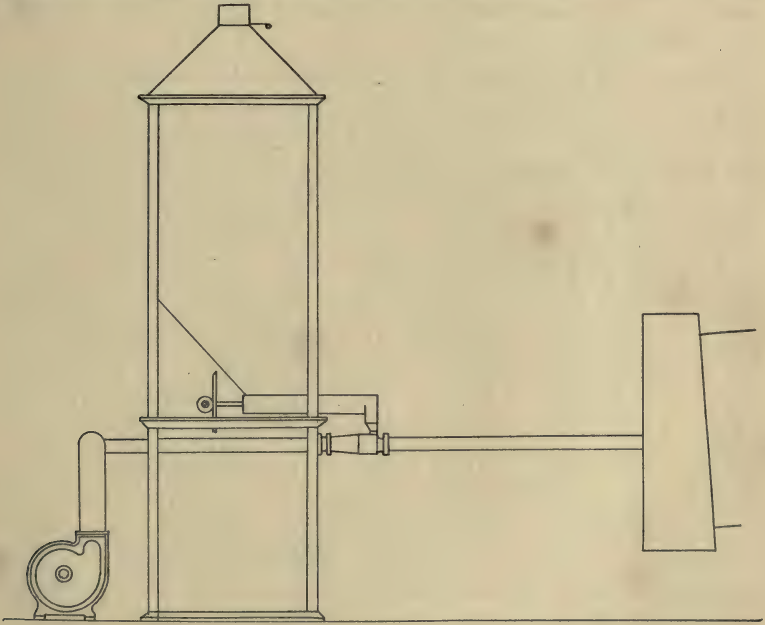

Fig. 25. Method of Burning Powdered Coal. (B. F. Sturtevant Co.)

experience that this will depend largely upon the material, how it burns, etc.

Fuel.

As we have said, during the early experiments with the rotary kiln, crude oil was used as a fuel. The growing scarcity and high price of oil led to the abandonment of this as a fuel and the substitution of powdered coal in its place. This practice became general about 1899, and since this cheap form of fuel was introduced, no new plants have been built which did not install rotary kilns, the objection to them previous to this being the high cost of the oil. The saving effected by the change was considerable, and only one or two plants in this country use crude oil, and these are situated near oil fields.

The method for burning the powdered coal is shown in Fig. 25. It consists of an injector through which air is forced by a fan. The coal is conveyed out of a bin by a screw conveyor, falls into the injector, is sucked in and mingles with the air as it passes through the pipe to the kiln. The injector is usually of cast iron, the pipe leading to the kiln is of galvanized iron and terminates in a nozzle of wrought iron pipe, which projects for a foot or more through the hood into the kiln. The screw conveyor leading from the bin is run usually by a line shaft independent of the kilns and usually attached to the fans or the motor driving the fans. The connection with the shaft is made either by some form of speed controller, or else by a stepped pulley, so the coal feed can be regulated. The air blown in is constant and is only a fraction of that needed for combustion. In some mills air from the compressors or high pressure air is used, and in others a combination of the two is sought. The main object in any event is merely to carry the coal into the kiln and to get a good mixture of coal and air.

Fig. 26 A shows the construction of an injector for use with low pressure air, and Fig. 26 B one for use with high pressure air.

The degree of fineness to which the coal is ground affects the amount of coal used directly, the finer the coal the less will be needed. Spackman stated in a paper read before the Association of Portland Cement Manufacturers that a fineness increase of 1%

over 75% through a 200-mesh sieve would effect a saving of 2% in fuel. This has been the experience, I believe, in other lines than cement in which powdered coal has been tried.

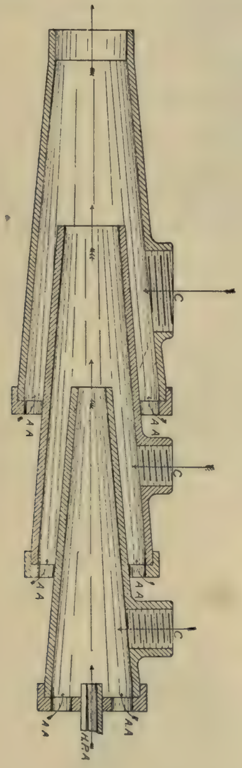

Fig. 26 A. High Pressure Coal Burner.
(C, coal ; H. P. A., high pressure air ;
A. A., atmospheric air.)

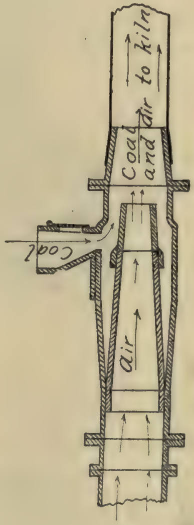

Fig. 26 B.

As to the fuel consumption of the rotary kiln, many reports seem to show that the 6x60-foot rotary kiln will require upon dry material from 96 to 110 lbs. of dry coal on an average, counting all the coal burned, including that for heating the kiln after patching and the usual enforced shut-downs and delays. Upon wet materials the coal consumption is from 140 to 160 lbs. per barrel. The extra coal being needed for the evaporation of the water of the slurry.

The coal for burning is usually gas slack and should fill the specifications below:

Volatile and combustible matter	30–45%
Fixed Carbon	45–60%
Ash not over	10%

Sulphur has no effect on the burning, except in large quantities. Iron pyrites are hard, and consequently may not pulverize. When coal containing much of this is used the pyrites may remain in coarse crystals after grinding, which are not blown in the kiln and burned, but fall from the nozzle of the burner among the clinkers and remaining unoxidized, are ground with the clinker, causing the resulting cement to develop brown stains. Practically none of the sulphur of the coal enters the cement, except as above.

Grinding the Coal.

The coal for burning is usually crushed in pot crushers or between rolls, dried in a special form of rotary dryer and finely pulverized in tube mills or Griffin mills. In some mills using a tube mill, this is preceded by a ball mill or a Williams mill; and in some, the coal is sent direct from the pile to the dryers and thence through the rolls.

One of the best forms of pot crushers is what is known as a "coffee-mill cracker." This is shown in Fig. 27. It works upon the same principle as a coffee-mill, and its action is a grinding one due to the toothed spindle, rather than a crushing one, and hence it can not choke up with soft material as a gyratory crusher would do.

When a set of rolls is placed before the dryer they are of the toothed form shown in Fig. 28 and can be used to crush run of mine coal. These rolls have a face about 30 inches wide and are usually about 24 inches in diameter. Where rolls are placed after the dryer to prepare coal for the tube mill they should, however, be plain-faced or very slightly corrugated. The toothed rolls will reduce coal to a size of 1 or 2 inch lumps and the plain-faced rolls will crush to lumps ranging from ½ inch down.

Three or four forms of coal dryers are in common use for drying coal for cement burning. The common form consists of a

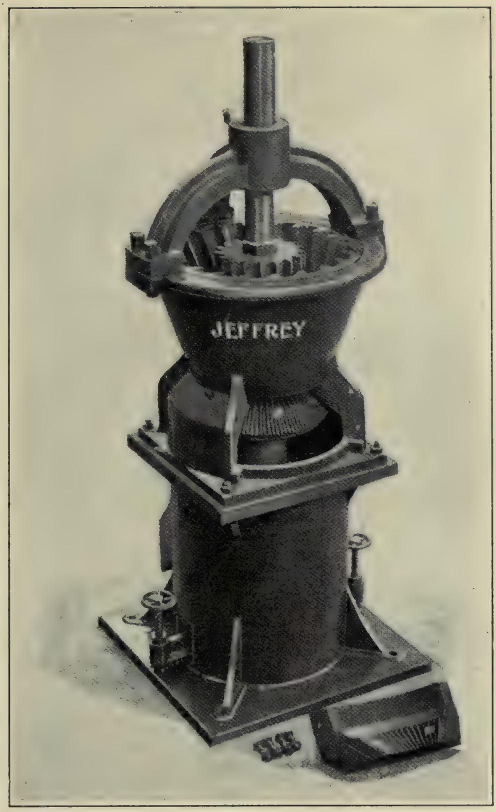

Fig. 27. "Coffee Mill Cracker" or Pot Crusher.

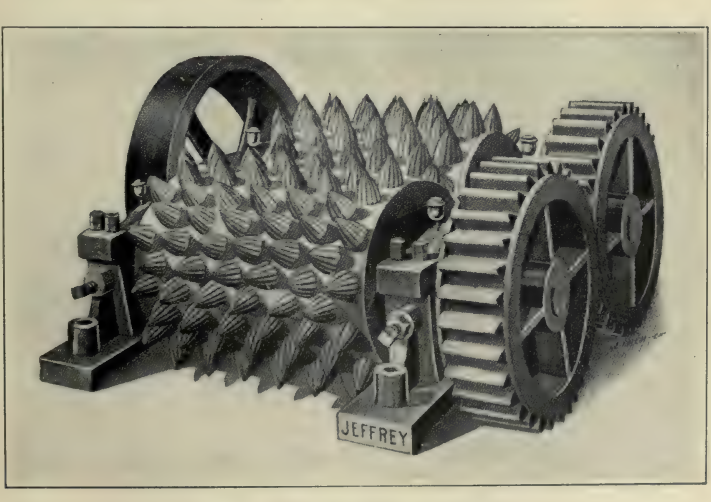

Fig. 28. Coal Crushing Rolls.

rotary cylinder provided with shelves, and in general similar to the dryers used for rock; except that it is encased in brick work and that the products of combustion pass around them and then, after cooling somewhat, back through them, instead of directly through them as with the rock dryers. Other forms of coal dryers are those manufactured by the F. D. Cummer & Son Co., The Ruggles-Coles Engineering Co., and The Bartlett & Snow Co.

The Ruggles-Coles dryer is shown in Fig. 29, and consists of two concentric cylinders, which are fastened together and revolve on steel tires, supported by bearing wheels. The cylinders are driven by gearing as shown. The inner cylinder extends beyond the outer one at the head end, and is connected with a brick furnace by a flue lined with fire brick. The products of combustion from the furnace pass down the central flue, and then back between the two cylinders. The coal is fed into the head end of the dryer between the two shells, and is caught up by flights on the inside of the outer shell and dropped on the hot inner shell. As the machine revolves the coal drops from the inner shell to the bottom of the outer one, is carried up by the flights and again dropped on the hot inner shell, etc., until dried. The hot gases of combustion passing up between the two shells also help to dry the material, which is discharged through the centre of the rear end. The fan is used to create a draft through the cylinders. These dryers are

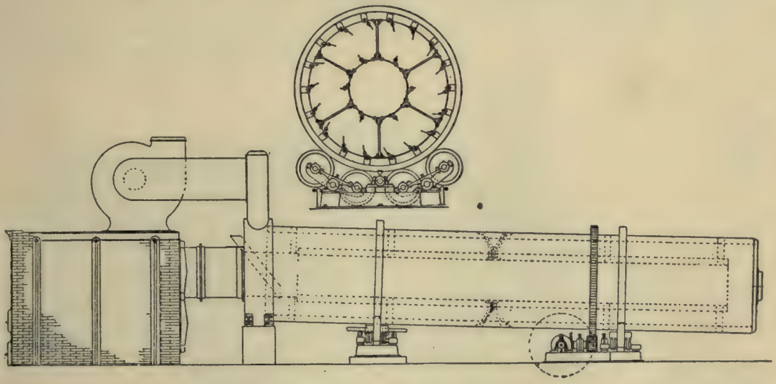

Fig. 29. Ruggles-Coles Dryer.

very economical and have been known to give as high economy as 7 to 8 lbs. of water evaporated per pound of coal burned.

The Cummer dryer is shown in Fig. 30. It consists of an iron cylinder entirely surrounded by a brick chamber. The cylinder is set at an incline and revolves on trunnioned bearings. It is provided with a great many hooded openings, *J*, so arranged that the heated air and gases of combustion are drawn into the cylinder by means of the fan, *G*. A furnace provided with a mechanical stoker produces the heat. The hot gases are drawn into the brick work chamber, where they are mingled with air drawn in through the registers, *E* and *O*, located at intervals in the brick work side of the chamber, and their temperature reduced by the dilution to a point making it safe for them to come in contact with the coal. The mingled air and gases of combustion are then drawn through the openings, *J*, and up through the cylinder. The material is fed into the cylinder through the hopper, *F*, and parts with its moisture as it works its way down through the cylinder to the discharge, *K*.

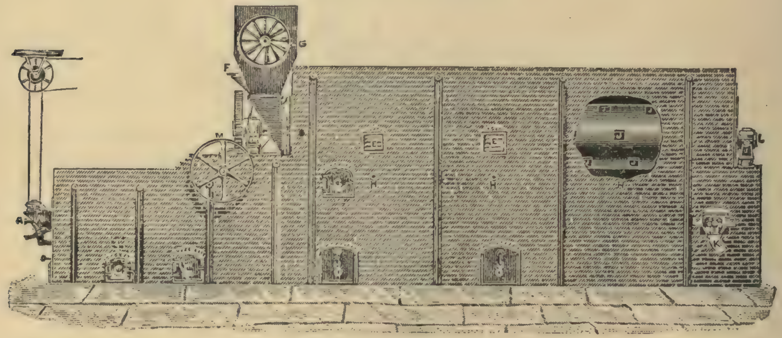

Fig. 30. Cummer Dryer.

At the plant of the International Portland Cement Co., Hull, Canada, the coal is dried by drawing air over the red hot cement clinker, and then through an ordinary dryer (such as is used for rock) with a fan. This serves to both cool the clinker and dry the coal.

When Griffin mills are used to pulverize the coal it is usual to reduce the latter to ½ inch size, though these mills are used occasionally on gas slack taking it just as it comes from the pile. Tube mills require the coal to be crushed by rolls or a crusher. In a few instances, ball mills have been installed to do this work, but have generally proved unsatisfactory from the frequency with which the outer screens clog. Two excellent mills for preparing coal for the tube mill are the Williams mill and the Stedman cage disintegrator. The Williams mill is shown in Fig. 31 and consists of hinged hammers which revolve rapidly around a horizontal shaft. These crush the material, and it passes out through a screen as shown in the cut.

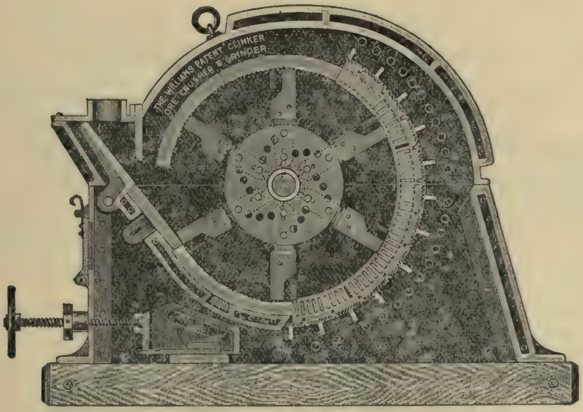

Fig. 31. Williams Mill.

Coal for burning Portland cement should be so finely ground that at least 92%, and better 95% of it, should pass a No. 100 sieve. The fineness is tested by sieving as directed for testing the fineness of cement, using shot to rap the coal through the sieve.

A Griffin mill will grind coal from rolls to a fineness of 95% through a 100-mesh screen at the rate of about 1½ to 2 tons per hour and at an expenditure of 20-25 horse-power. A 5′ 6″x20′ tube mill will grind enough coal for a six kiln plant, or about 2½ tons per hour, taking coal ranging from ½ inch lumps down, and using 80 horse-power in doing so. The Williams mill is made in several sizes and one large enough to prepare coal for two tube mills can be obtained. The capacity of a coal grinding plant will depend entirely on the condition in which the coal is received at the mill and the thoroughness with which the coal is prepared for the tube mill or Griffin mill. The tube mill is not well adapted to crushing coarse material and where it is used considerable economy will be effected by reducing the coal to ¼ inch or finer by means of some form of disintegrator such as a Williams or Stedman mill. When run of mine coal is received, the best treatment would be by a set of toothed rolls before the dryer, then the dryer, followed by a disintegrator and a tube mill or by a set of plain-faced rolls and a Griffin mill.

In order to avoid dangerous explosions in coal mills, the roof should be so ventilated that there can be no accumulation of gases here. The precautions about lights, fire, smoking by the operators, etc., that are usually taken in connection with inflammable materials should also be observed. When tube mills catch on fire inside, the fire may be smothered with steam; or a 20-lb. drum of liquid carbon dioxide gas may be kept and used for this purpose. The mill must be well cleared of this gas, however, before workmen are allowed to enter it to prevent their asphyxiation. Water is ineffective and should not be used as it merely stirs up a dust, and mixtures of coal dust and air are very explosive.

O. A. Done, writing in *Engineering News,* gives the following hints on the prevention of spontaneous ignition in coal piles. The amount of moisture in a bituminous coal is a measure of the risk of spontaneous combustion when the fuel is stored. Bituminous coal should not contain more than 4.75 per cent. water. Coal bins should be of steel or iron protected by concrete and should be roofed over. Free air passages should be provided around the walls and beneath the bins to keep the pile cool, and the depth of the coal should never exceed 12 feet. It is useless to provide air passages in the body of the pile as these only tend to promote oxidation; similarly cracks, etc., in the walls of the fuel bin increase the risk.

Burning with Natural and Producer Gas.

Natural gas has been successfully used for the heating of the kiln, both at Iola, Kan., and at Wampum, Pa. At the former place the gas is also used to generate power for grinding, etc., in gas engines. Producer gas has been tried but the writer knows of but one plant where it has been used for any great length of time, that is at a small plant in Canada. In conversation, the manager of this plant informed the author that they considered it as cheap as powdered coal, but saw no particular advantage in its use. The question has been raised at numerous times as to whether sufficient heat could be developed by its use to secure the proper temperature in the kiln for burning, and numerous calculations have been given to prove that without regeneration producer gas could not be used for burning Portland cement. The fact that it is used at this plant should effectually set at rest this contention. At this plant, the producers are located directly in front of the kilns and below the kiln floor, the gas being conducted to the kiln by a short pipe.

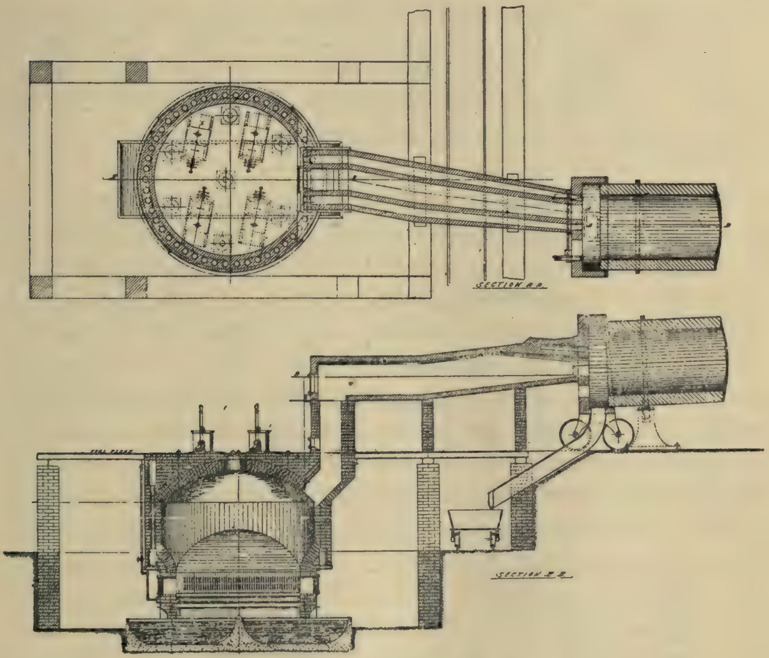

Fig. 32. Swindell Gas Producer and Rotary Kiln.

The Diamond Portland Cement Co., Middle Branch, O., has also had a Swindell gas producer in operation heating one of their kilns for over a year and they report very favorably upon its use. Fig. 32 shows the installation of the producer at this plant. The gas producer is built 15 feet in front of the kiln, which is 6 feet in diameter and 60 feet long. The coal, which is of inferior quality and costs only $1.50 per ton, is introduced into the producer by means of sliding hoppers. Steam and air are introduced under and through the inclined grates by means of blowers. The air used for combustion is preheated by passing up through iron tubes built in the walls of the producer. The air and gas are led to the kiln by separate flues as shown in the plan. The labor required to operate the producers amounts to about 3½ cents per barrel of cement including the wages of the burners, the coal consumption amounts to 130 lbs. per barrel and the output to 240 barrels per day.

The producer, however, has not yet reached anything near like perfection. The development of the gas engine will also have a direct bearing on the question. If this should be brought to the point where it would displace steam, the gas producer would be much improved and the possibility of generating gas for burning and for power in one and the same plant, doing away with boilers and coal grinding machinery, would undoubtedly influence manufacturers largely in putting in producers. The gas engine is being perfected rapidly and results obtained in Europe lead one to believe its commercial perfection will be shortly accomplished.

Mr. H. F. Spackman, in a paper read at a meeting of the Cement Manufacturers' Association, stated that in a plant designed by his company producers were tried in connection with powdered coal on two rotary kilns, 60 feet long by 5 feet in diameter, burning slurry containing 60% water. Actual figures in this plant obtained on a two or three months' run, were 125 barrels of cement per day, with a coal consumption of 135 lbs. of coal per barrel, while the kilns working on powdered coal required on an average for a seven months' run 138 lbs. of coal per barrel. To greatly overbalance this 3 lbs. saving in coal, however, was the fact that six men each shift of 24 hours were required to work the producers and that as gas slack could not be employed a coal costing 50 cents more a ton had to be substituted.

Natural gas is used for burning cement at several plants in Kansas. Its use has passed beyond the experimental stage and where it is obtainable it is of course the cheapest form of fuel. Natural gas is, however, found in too few localities to make it generally applicable to cement burning, and, even when found, the supply is limited and may give out after a few years. Below are analyses of the gas at Iola, Kans., and at Independence, Kans., at both of which places Portland cement mills are using natural gas not only for heating the kilns but also for generating power.

ANALYSIS OF NATURAL GAS USED FOR BURNING PORTLAND CEMENT IN KANSAS (BAILEY).[1]

	Iola.	Independence.
Hydrogen	0.00	0.00
Oxygen	0.45	trace
Nitrogen	7.76	3.28
Carbon Monoxide	1.23	0.33
Carbon Dioxide	0.90	0.44
Ethylene Series	0.00	0.67
Marsh Gas	89.66	95.28

Kiln Lining.

The rotary kiln as has been said is lined with fire brick. This brick should be of the most refractory kind. I believe at one time a magnesia brick was used but now a good quality fire brick is considered as satisfactory and more economical than the expensive magnesia lining. A good fire brick should analyze within these limits:—

	Per cent.		Per cent.
Silica, SiO_2	45.0	to	50.0
Alumina, Al_2O_3	43.0	to	48.0
Iron, Fe_2O_3	Less	than	3.0
Magnesia, MgO	"	"	0.5
Lime, CaO	"	"	0.5

It should also be free from iron and alkalies, since these cause fusibility. A fire brick lining should last, if carefully attended to, at least 9-12 months and sometimes they go even longer than this.

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[1] Mineral Resources of Kansas for 1897.

At the end of this time the bricks are eaten away nearly to the iron shell and it becomes necessary to take away the brick from the first 20 or 30 feet of the kiln and reline this portion. The upper part of the kiln lining, or that portion of it which merely comes in contact with the powdered raw material before sintering commences, usually lasts indefinitely. In kilns working on wet materials it is sometimes the practice to leave the upper 20 or 25 feet of the kiln unlined since this part of the kiln is kept fairly cool by the wet slurry. Sometimes channel irons or z bars are fastened to the sides of the kiln to form shelves for drying the material.

In place of fire brick a concrete or clinker brick made from Portland cement clinker and Portland cement is used. The clinker should be screened and that portion of it passing a ¼ inch screen used. This is mixed with Portland cement in the proportions of thirty parts clinker to twelve parts cement and made into a medium wet concrete. This is then rammed into wooden forms of the proper size and shape and allowed to harden. The bricks are ready for use several days after making. One large mill in the Lehigh District used these bricks exclusively at one time for lining the clinkering zone of their kilns, and found them very satisfactory. Under conditions in this region, however, they do not seem to be any cheaper than fire brick.

The fire bricks used to line the lower end of the kiln are usually from 9 to 12 inches thick, and those for lining the upper end, from 4 to 6 inches. These bricks are keyed to fit the circle of the kiln.

It is sometimes the practice to place a lining of sheet asbestos between the fire brick lining and the steel shell. This protects the tires, and also the shell, to some extent, as it cuts off some of the heat transmitted to the latter. The writer has used an asbestos lining several times and found that it unquestionably cuts off some heat from the shell. In lining the kiln with asbestos, ¼ inch board is usually used.

In the old upright kilns it was the usual practice to coat the lining of the kiln with a "grout" of slurry, so that it was natural for something of the same sort to be tried upon the rotary kiln. It was soon found that a certain amount of the raw material could be made to adhere to the fire brick lining of the kiln, thereby removing the bricks from the scorrifying action of the caustic clinker. It is now the practice to burn entirely on coated bricks. When this coating falls off, usually only in patches, the kiln is heated up, raw material is scraped down over the bare spot and pounded into place with a heavy iron bar. Water is then usually run on the "patch" to harden it. In some mills salt is used on the bare spot, as it is supposed to make the patch hold better. The writer has never seen any advantage in its use, however.

The fire brick are held in the kiln by a heavy angle iron running around both ends of the kiln. This also helps to stiffen the kiln shell.

The operation of Portland cement burning is essentially a skilled process and a skilled workman is required to attend it. He must know just how the clinker should be burned and have a good eye for "heat," so that he can tell when his kilns are hot enough to clinker the raw material properly. The placing of the patches and the coating of a freshly lined kiln also require some skill. To be economically run the kilns should be kept at as nearly a uniform temperature as the irregularity of the feeding devise will permit. Kilns run spasmodically, first hot, then cold, require much coal, turn out poorly burned clinker, and require much patching. Since patching requires the stopping of the kiln the output is also cut down.

The burner should also be a sufficiently good mechanic to look after the mechanical part of his kilns. One burner usually looks after two kilns. The operations of the interior of the kiln are watched through darkened glasses. No efforts have been made to use pyrometers since the temperature must change with the refractoriness of the material and the heat is entirely judged by the incandescence of the interior of the kiln and the clinker as observed through these glasses.

Chemical Changes Undergone in Burning.

The changes undergone during burning may be summed up as follows:

The carbon dioxide, existing in the raw material in combination with the lime and magnesia as carbonate of these elements, is practically entirely expelled. Even the little which exists in freshly ground, well burned cement is probably most of it absorbed from the air, since cement very rapidly absorbs carbon dioxide and water.

All of the water originally present whether free hygroscopic or combined is driven off and the carbon and organic matter in the raw material are also burned away. The iron, the greater part of which is usually present in clay and cement rock in the ferrous condition, is almost completely oxidized.

The sulphur whether present in the raw material as sulphide, sulphate or in combination with organic matter is much of it expelled and the remainder is usually all of it, except a mere trace, found present as calcium sulphate. This is to be expected since calcium sulphate gives off its sulphuric acid, when heated with silica. Indeed, I believe it has been proposed to make cement by heating together a mixture of clay and gypsum, the sulphuric anhydride driven off during the process being caught and condensed with water and sold for sulphuric acid. It has also been supposed that the sulphur of the coal entered the clinker. This is erroneous, since the amount of gas slack necessary to burn 100 lbs. of clinker will contain sufficient sulphur to make the clinker analyze at least 1.5 per cent. SO_3 if it were all absorbed, while as a matter of fact clinker seldom analyzes anywhere near this amount.

The alkalies, potash and soda are partly expelled in the kiln. In experiments made by the writer, which will be detailed below, the losses of soda amounted to from 19 to 28 per cent., while those of potash ran from 46 to 52 per cent. W. F. Hillebrand, of Washington, D. C., has applied for a patent on a process for condensing these alkalies, looking to their utilization as fertilizers. This loss of alkali is also shown by analysis of the deposit collecting on the walls of the kiln stack, a sample of which contained

	Per cent.
Soda	1.38
Potash	6.83

In a paper read by the author before the Association of Portland Cement Manufacturers, the results of an experiment to determine the losses actually occurring in the rotary kiln were given. This experiment consisted in sampling carefully the raw material going into the kiln, the clinker coming out and the coal used for burning. The samples were taken every 3 minutes for 5 hours. The clinker was not sampled for 45 minutes after the first raw material sample was taken and was collected for 45 minutes after the last raw material sample was taken; the idea being to allow the material to work through the kiln so that the clinker represented the burned raw material. The samples were taken on kilns working normally, with a steady feed and raw material of constant composition. The samples were then all carefully analyzed. Three separate tests were made, but only one set of results is given here:

	Raw material as analyzed.	Clinker as analyzed.	Raw material calculated to a clinker.	Clinker calculated without its H_2O, CO_2, etc.	Loss or gain
SiO_2	13.44	21.06	20.47	21.14	+67
TiO_2	0.23	0.32	0.35	0.32	—03
Al_2O_3	4.55	7.29	6.93	7.32	+39
Fe_2O_3	0.56	2.52	2.34	2.66	+32
FeO	0.88	0.11	...	...	...
MnO	0.06	0.09	0.09	0.09	00
CaO	41.84	63.55	63.72	63.80	+08
MgO	1.94	2.95	2.94	2.97	+03
Na_2O	0.31	0.38	0.47	0.38	—09
K_2O	0.72	0.59	1.10	0.59	—51
P_2O_5	0.22	0.34	0.34	0.34	—00
SO_3	...	0.30	1.25	0.38	—87
S	0.33	0.03	...	...	...
C	0.75	...	...	...	...
CO_2	32.94	0.32	...	...	...
H_2O	1.55	0.24	...	...	...

In the second and third columns will be found the analysis of the raw material and clinker respectively. In the fourth column is calculated the composition the raw material would have after clinkering if the only changes which took place were the oxidation of the ferrous iron and sulphur, the burning off of the carbon and the volatilization of the carbon dioxide and water. The fifth column gives the analysis of the clinker calculated to 100% without its water and carbon dioxide and after its sulphur and iron had all been calculated to SO_3 and Fe_2O_3 respectively. The coal used for burning in the experiment was Fairmont gas coal.

Analysis of Fairmont Gas Coal:

Moisture		1.34
Volatile and combustible matter		34.11
Fixed carbon		54.03
Ash— SiO_2	3.59	
TiO_2	0.08	
Al_2O_3	1.50	
Fe_2O_3	1.91	
MnO	0.03	
CaO	0.75	
MgO	0.03	
Na_2O	0.10	
K_2O	0.16	
P_2O_5	0.06	
SO_3	0.54	
		8.75
Sulphur		1.77

Twenty-nine pounds of this coal, the quantity generally considered necessary to burn 100 pounds of clinker, will contain:

	Pounds.
SiO_2	1.04
TiO_2	0.02
Al_2O_3	0.44
Fe_2O_3	0.55
MnO	0.01
CaO	0.22
MgO	0.01
Na_2O	0.03
K_2O	0.05
P_2O_5	0.02
SO_3 (total S to)	1.43

If we compare these figures with those in the last column of the table, we will see that the silica, ferric oxide and alumina have been increased by approximately one-half the coal ash. Undoubtedly, in the rotary kiln much of the ash is carried out with the gasses by the strong draft of the kiln. This we would expect when we consider that the particles of ash are of the same volume as the particles of coal, and yet only one-tenth their weight, for when the coal burns it leaves its ash in the form of a skeleton. These particles of ash are already in motion and are in the full draft. The gases have a velocity of at least 2,000 feet per minute, which is quite enough to carry the particles up the chimney. It seems probable in view of these facts that what ash does contaminate the clinker, comes from the impinging of the flame upon the material in the kiln. The ash strikes the clinker and its velocity is stopped by the impact and it either falls among the clinkers or it sticks to the red hot, semi-pasty mass. It is probable that the coarser the coal the more ash will contaminate the clinker. It is an important point where this ash falls. If it falls before the raw material begins to ball up, 24 lbs. extra limestone should be added to every 600 lbs. of raw material to take care of the ash, as in this case, it would form Portland cement clinker. If, however, it falls on the clinker after it forms into balls, this quantity should be very much less, if any at all, as its action is merely on the surface of the clinker to form a slag and not a true Portland cement clinker.

If we recalculate the clinker, taking into consideration the volitilizing of the sulphur, potash and soda, and adding one-half the elements introduced by the coal ash, we would have a clinker with the following analysis:

SiO_2	21.09
TiO_2	0.36
Al_2O_3	7.17
Fe_2O_3	2.62
MnO	0.09
CaO	63.99
MgO	2.95
Na_2O	0.39
K_2O	0.61
P_2O_5	0.35
SO_3	0.38

Comparison of these figures with those of the fifth column shows them to be very close to our actual results.

Another point brought out by these tests is the loss of material, as dust, etc., during the pulverizing and burning of the raw material and clinker. Allowing the losses shown for volatilization of the soda, potash, and sulphur, in the proportions shown in the experiment, and adding one-half of the coal ash, 100 lbs. of raw material should make 67.25 lbs. of clinker, or 565 lbs. of raw material should make 1 barrel, or 380 lbs. of clinker. The rock as it comes from the quarry usually carries much more moisture than the analysis shows, but even taking an extreme of 5% moisture, 594 lbs. should make a barrel of clinker. Few manufacturers use less than 610 lbs., showing a lost of 16 lbs., as dust, etc., per barrel of clinker produced.

The above changes are simply those which we can detect by comparative chemical analysis of the raw material and the clinker. None of them are sufficient of themselves to form Portland cement. All the carbon dioxide can be driven off the raw material and still Portland cement clinker will not be the result. For this it is necessary that the lime combine with the silica and the alumina, and in order for this combination to take place it is necessary for the material to be heated to a considerably higher temperature than that necessary to drive off carbon dioxide. If a small sample of raw material is heated to a constant weight over an ordinary laboratory blast lamp, very little, if any, clinkering will take place, except, perhaps, on the under side of the sample next to the crucible, yet all the carbon dioxide will have been driven off. The various opinions as to the constitution of Portland cement clinker have been fully detailed in Chapter II on the chemical composition of Portland cement, and it is unnecessary here to repeat them. W. B. Newberry's experiment on the various stages of burning given below, and E. D. Campbell's researches as to clinkering temperatures, also outlined further on, have done something to advance our knowledge of cement burning.

Wm. B. Newberry's experiment[1] is of great interest as tend-

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[1] *Cement and Engineering News*, Vol. XII, No. 5.

ing to throw some light on the question of what takes place during the passage of the raw material through the kiln.

During a temporary shut down of one of the rotaries at the Dexter Portland Cement Co., at Nazareth, Pa., the kiln was allowed to cool down without being emptied and samples of the charge were then taken from every four feet throughout the length of the kiln.

After careful examination these samples were analyzed, the results showing the changes which take place in the composition at successive stages of the burning. The raw material used was cement rock without the addition of any other material. The first sample was of unburned raw material taken at the point of entering the kiln and the last (No. 14) was the finished clinker within four feet of the discharge at the lower end.

Below is given a table of the successive analyses:

No.	SiO_2.	Fe and Al.	CaO.	MgO.	Loss on ignition.
1	13.70	6.00	42.12	1.97	35.30
2	13.65	5.58	41.95	1.96	35.04
3	14.38	5.70	41.63	1.88	34.84
4	13.55	6.30	41.98	2.12	23.46
5	14.33	6.27	44.05	1.65	32.76
6	14.46	6.36	44.67	1.89	30.56
7	14.90	6.55	46.19	2.30	28.38
8	16.44	6.99	49.25	2.33	24.94
9	17.03	7.80	53.04	2.30	18.44
10	17.94	8.50	56.20	2.35	13.04
11	18.60	9.04	59.00	2.70	8.32
12	18.66	9.75	62.68	2.80	4.34
13	19.90	10.76	63.38	2.83	1.08
14	20.36	10.78	63.76	2.81	0.86

The samples were finely ground and analyzed after strongly igniting and dissolving in half strength hydrochloric acid.

"It will be seen from this that the process of burning in the rotary takes place, not, as has been supposed, in a series of steps, but in a continuous change, the moisture and organic matter beginning to pass off as soon as the raw material attains the temperature of the upper end of the rotary, shown by the change in color from blue gray to light buff or cream color between 3 and 4. The carbonic acid soon follows; Nos. 4 and 5 at 16 and 20 feet showed marked loss. As the carbon dioxide burns off, the proportions of the solid elements rise steadily, the greatest variations being shown from 8 to 12, when the temperature passes from a bright red to a white heat. The whole of the volatile matter is, however, not driven off until the clinker is completely burned and about to leave the kiln, at which point but .86% remains.

"Much of interest may be deduced from these results.

"The physical change from raw stone to clinker is shown by the characteristics of the different samples given below:

"Nos. 1, 2 and 3, blue gray powder, changing to buff between 3 and 4.

"Nos. 4, 5 and 6, yellowish buff powder commencing in 6 to ball up into small lumps.

"Nos. 7, 8, 9 and 10, yellow to brown balls like marbles; soft, easily crushed in the fingers, becoming darker and harder toward 10.

"No. 11, lumps quite hard and dark brown, traces of sintering on surface, softer inside.

"No. 12, lumps brown and partly sintered, beginning to lose regular rounded form, hard.

"No. 13, larger lumps, irregular and rough, almost black. Very noticeable difference between 12 and 13, latter is like brownish clinker and is burnt throughout.

"No. 14, smaller and more rounded lumps, black, has all the appearance of finished clinker, in fact no further change is seen as it leaves the rotary.

It is to be hoped that the experiment will be repeated and microscopic sections made of the various samples of clinker. This would throw still more light upon the question.

Campbell made numerous experiments in burning mixtures of marl and clay in varying proportions in a small rotary kiln[1]

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[1] *J. Am. Chem. Soc.*, XXIV, 248.

fitted with a Le Chatelier pyrometer and observing the properties of clinker formed at various temperatures. From these experiments he fixed the temperature, necessary to properly burn most commercial cements at 1550° C or 2822° F., while high limed cements would require an even greater temperature. For example[1]; he found a mixture of clay and marl in which the ratio of the silicates ($SiO_2 + Al_2O_3 + Fe_2O_3$) was to the lime ($CaO$) as 100:228.8, and which gave a clinker containing 62.64 per cent. lime, to require a temperature of 1549° C. for proper burning, while a mixture of the same clay and marl in which the silicate-lime ratio was 100: 240.8 and which gave a clinker analyzing 63.83 required a temperature of 1593° C. A third mixture of these materials having a silicate-lime ratio of 100: 266.4 and giving a clinker analyzing 66.12 per cent. lime failed to burn perfectly even at 1625° C.

This, of course, corroborates the experience of every cement chemist, that the higher the lime, other things being equal, the higher temperature is needed to burn it.

In the same series Campbell also found that the mixture of clay and marl with the silicate-lime ratio of 100: 228.8, which required a temperature of 1549° C for proper burning could be burned at a temperature of 1478° C by revolving the kiln more slowly. This again corroborates the experience of manufacturers, that a longer time in the kiln would do the same work as a much higher temperature.

In a second experiment[2], Campbell and Ball investigated the influence of fine grinding of the raw materials on the clinkering of cement. A mixture of cement rock from the Lehigh District, as ground ready for the kiln by a prominent mill of this region, was subjected to a sieve test and found to run 72.4 per cent. through a 200-mesh sieve and 85.6 per cent. through a 100-mesh sieve. This mixture could not be thoroughly burned even at 1612° C., but when reground so that 98 per cent. of it passed a 200-mesh sieve proper, burning was accomplished at a temperature of 1475° C or 137° C less. This experiment is valuable as showing the importance of fine grinding in fuel economy. While

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[1] *J. Am. Chem. Soc.*, XXIV, 969.

[2] *J. Am. Chem. Soc.*, XXV, 1103.

it would probably be impracticable to grind hard raw materials to a fineness of 98 per cent. through a 200-mesh sieve, it is practicable and indeed is usual to grind more than 85 per cent. through a 100-mesh sieve.

While there is no definite information to that effect it is generally accepted as a fact that the presence of alkalies lower the temperature at which clinkering takes place. In a small furnace which the writer had he could never quite get the temperature up to the point for a thorough burning of the Lehigh cement rock-limestone mixtures, but if the small cubes of powdered material were made up with water containing enough sodium carbonate to make the mixture analyze about 1.5 per cent. soda, the clinkering could easily be accomplished.

Iron also plays an important part in aiding the clinkering. Various experimenters who have endeavored to make white cement by the use of iron free clays and marl or limestone have found it hard to clinker the material properly and have gotten around the difficulty usually by addition of alkali in the form of feldspar. Fluorspar or calcium fluoride, CaF_2, has also the effect of lowering the clinkering temperature and has been used, commercially, for that purpose, I believe.

Degree of Burning.

Properly burned Portland cement clinker is greenish black in color, of a vitreous lustre and usually when just cooled sparkling with little bright glistening specks. It forms in lumps from the size of a walnut down, with here and there a larger lump. Underburned clinker, whether this is due to a low temperature in the kilns or an overlimed, mixture lacks the vitreous lustre and the glistening specks. The *failure* to sparkle, however, is not necessarily characteristic of underburned clinker, though the sparkle itself is never seen in underburned clinker, as the rate of cooling etc., effects this somewhat. If much underburned, the clinker is brown, or has soft brown or yellow centres. Low limed clinker unless very carefully burned, usually has brown centres also, but is hard and glassy. The two should not be mistaken; the clinker with *soft* brown centres is underburned that with *hard* brown centres is underlimed.

Overburned clinker shows the same characteristic as underlimed,—the hard brown centres. I have never seen that the quality of cement was injured any by overburning, unless the material was low in lime when the resulting cement was apt to be "quick setting," but the proper degree of sintering is far enough to carry the process and to burn any harder is not only a waste of coal for burning, but also for grinding since the hard brown slag like clinker is very hard to pulverize. Properly burned clinker should have a specific gravity of at least 3.15 and when rapidly pulverized and ignited show a loss of under 1 per cent.

Thermo-Chemistry of Burning.

These chemical changes or reactions either give off or require heat. If the former they are exothermic, if the latter endothermic.

The exothermic or heat generating reactions are the burning of the sulphur and carbon (organic matter) of the raw materials. The endothermic or heat absorbing ones are the decomposition of the calcium and magnesium carbonates.

The combination of the lime with the silica and alumina is also thought to be an exothermic reaction, but authorities differ on this point.

The quantity of heat generated by chemical reaction or required to bring it about is usually expressed in terms of one of two units. These are the *British Thermal Unit, usually* abbreviated to B. T. U. and the *Calorie* sometimes abbreviated to Cal. The British Thermal unit is the heat required to raise the temperature of one pound of pure water through one degree Fahrenheit at or near 39.1° F., the temperature of its maximum density. The Calorie is the heat necessary to raise the temperature of one kilogram of water from 4° C. to 5° C. A calorie is equivalent to 3.968 B. T. U., and a B. T. U. to 0.252 Calorie. The B. T. U., however, produced by the oxidation or combustion of one *pound* of a substance is $^9/_5$ of the number of Calories which would be produced by one kilogram of the substance. Hence, to reduce Calories per kilogram to B. T. U. per pound multiply by $^9/_5$ while to change B. T. U. per pound to Calories per kilogram multiply by $^5/_9$.

The British Thermal Unit is the one generally used by engineers for expressing the heating value of fuel while the calorie is used in most scientific calculations.

The following are the heat values of the reactions mentioned above:

	B. T. U.
1 pound of carbon burned to CO_2 gives off	14,540
1 pound of sulphur burned to SO_2 gives off	4,050
1 pound of $CaCO_3$ decomposed into CO_2 and CaO requires	784[1]
1 pound of $MgCO_3$ decomposed into CO_2 and MgO requires	384[1]
1 pound of CaO uniting with SiO_2 and Al_2O_3 gives off	1064[1]
0.56 pound of CaO, equivalent to 1 pound of $CaCO_3$ uniting with SiO_2 and Al_2O_3, gives off	596[1]

	Calories.
1 kilogram of carbon burned to CO_2 gives off	8,080
1 kilogram of sulphur burned to SO_2 gives off	2,250
1 kilogram of $CaCO_3$ decomposed into CO_2 and CaO requires	436[1]
1 kilogram of $MgCO_3$ decomposed into CO_2 and MgO requires	213[1]
1 kilogram of CaO uniting with SiO_2 and Al_2O_3 gives off	591[1]
0.56 kilogram of CaO, equivalent to 1 kilogram of $CaCO_3$. uniting with SiO_2 and Al_2O_3 gives off	331[1]

As I have said there is some doubt about the heat given off by the combination of the lime with the silicates, and this point needs investigation. It is the one stumbling block to our calculating the efficiency of the rotary kiln. As it seems probable that the reaction does give off some heat, though the amount is probably very small, we can arrive at the maximum heat theoretically required to burn a barrel of cement, or rather the heat from outside sources absorbed by the chemical reactions.

As we have said heat is required to decompose the carbonates and is given off by the burning of the carbon and the sulphur of the mix[1]. The raw material of the Lehigh District contains per 100 pounds, about

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[1] Berthelot, Thermochemie, Vol. II. These values are dubious.

[2] If the sulphur of the mixture is present as sulphide, it burns, giving off heat. If present as sulphate, heat is required to expell it (1890 B. T. U. per pound.)

	Pounds.
Carbonate of lime	75.0
" " magnesia	4.0
Carbon	0.8
Sulphur	0.3

Hence, there would be required heat as follows:

	B. T. U.	B. T. U.
To decompose 75 lbs. of $CaCO_3 = 75 \times 784$	58,800	
To decompose 4 lbs. of $MgCO_3 = 4 \times 384$	1,536	60,336
There would be given off:		
By burning of 0.3 lbs. of sulphur $= 0.3 \times 4050$	1,215	
By burning of 0.8 lbs, of carbon $0.8 \times 14,540$	11,632	12,847
Balance to be supplied by fuel		47,489

Since 1 barrel of cement requires about 600 lbs. of dry material it would require $47,489 \times 6$ B. T. U., or reckoning 1 lb. of Fairmont gas slack at 14,000 B. T. U., 1 barrel of cement would require $\frac{47,489 \times 6}{14,000}$ or 20.35 lbs. of coal.

If we consider, however, that heat is given off by the combination of the lime with the silicates, then this heat would amount to $75 \times 596 = 44,700$ B. T. U. Subtracting this from 47,489 would leave only 2,789 B. T. U. to be supplied by the coal or $\frac{2,789 \times 6}{14,000}$ $= 1.2$ lbs. of coal per barrel. This latter figure seems hardly probable.

Of course, the figure 20.35 lbs. of coal per barrel is an ideal one, and in order to realize it in practice we would have to recover all the heat not actually utilized in the chemical reaction. We would have to cut off all radiation from the kiln, the clinker and flue gases would have to leave the kiln at the temperature of the air, and we would have to condense the water evaporated from the mix and recover the heat units expended upon it.

Of course, it is impossible to do this economically. There will always be some loss by radiation, and the water must leave the kiln at a temperature above its boiling point. We must also have sufficient difference between the temperatures of the waste gases and the outside air to produce natural draft. Table XVIII shows the various constants necessary to calculate the heat carried off by the kiln gases and the clinker.

TABLE XVIII.—CONSTANTS[1], ETC., FOR USE IN CALCULATING THE HEAT LOSSES OF THE ROTARY KILN.

	Pounds
Weight of air necessary to burn one pound of—	
Carbon (to CO_2)	11.6
Hydrogen (to H_2O)	34.8
Sulphur (to SO_2)	4.4

Weight of products of combustion from one pound of—		
Carbon	$CO_2 = 3.66$ lbs.	$N = 8.94$ lbs.
Hydrogen	$H_2O = 9.00$ lbs.	$N = 26.8$ lbs.
Sulphur	$SO_3 = 2.00$ lbs.	$N = 3.35$ lbs.

	B. T. U.
Heat required to evaporate 1 lb. of water	996
Specific heat of products of combustion of 1 lb. of gas slack coal	0.250
Specific heat carbon dioxide	0.234
" " carbon monoxide	0.245
" " nitrogen	0.244
" " air	0.238
" " steam	0.480
" " water	1.000
" " clinker	0.246

Below is an analysis of Fairmont gas slack coal (such as is used in the Lehigh District) made by the writer:

Water (110°C.)	1.9
Carbon	74.9
Hydrogen	4.8
Oxygen	8.6
Nitrogen	1.4
Sulphur	0.7
Ash	7.7
	100.0

Neglecting the sulphur which is present only in very small amount the combustible elements in 100 lbs. of this coal are 74.9 lbs. of carbon and 4.8 lbs. of hydrogen. Of this hydrogen, however, $\frac{8.6}{8}$ lbs. will be needed for the oxygen of the coal itself, leaving only $(4.8 - \frac{8.6}{8} = 4.8 - 1.1 = 3.7)$ to require outside oxygen; hence, to burn 100 lbs. of this coal will require

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[1] These constants are of course mere approximations, but are sufficiently near the truth for rapid calculations of heat losses.

For the carbon	$74.9 \times 11.6 = 869$ lbs. air
For the hydrogen	$3.7 \times 34.8 = 129$ " "
Total for 100 lbs. coal	$= 998$ " "
Total for 1 lb. coal	$= 10.0$ " "

The products of combustion from 100 lbs. of coal would of course weigh 998 lbs. + combustible and volatile part of the coal or $998 + (100 - \text{ash})$.

Therefore, products of combustion from 100 lbs. of coal would weigh $998 + (100 - 7.7) = 1090$ and products of combustion from one pound of coal 10.9 lbs.

Now neglecting the unimportant elements:—

The combustion of 74.8 lbs of carbon will produce:	$74\ 8 \times 3.66 = 274$ lbs. of CO_2.
And	$74.8 \times 8.94 = 669$ " N.
The combustion of 3.7 lbs. of Hydrogen will produce:	$3.7 \times 9 = 33$ " H_2O.
And	$3.7 \times 26.8 = 99$ " N.

Now there are 1.9 lbs. of water from the moisture of the coal and $8.6 + \frac{8.6}{8} = 9.7$ lbs. from the oxygen of the coal, hence there will be in the products of combustion from 100 lbs. of coal 768 lbs. of nitrogen, 274 lbs. of carbon dioxide, and 44.6 lbs. of water.

Hence, the mean specific heat of the gases will then be:—

Nitrogen	$768 \times .244 =$	187.4
Carbon dioxide	$274 \times .234 =$	64.1
Water (steam)	$45 \times .48 =$	21.6
	1087	273.1

$$\text{Mean specific heat} = \frac{273.1}{1087} - 0.251.$$

This figure may be taken as fairly representative of the specific heat of the products of combustion from gas slack coal. It is of course not a very exact figure because the specific heat of gases increases slightly with their temperature. It is probably exact enough for ordinary purposes, however, since in most calculations of this sort so much is assumed that very exact figures are merely a waste of mathematics.

Numerous tests of the waste gases of the rotary kiln working on dry material under normal conditions show a temperature at the mouth of the kiln of from 1500° F. to 2200° F. Analysis of these gases also show some excess of air, not so much as sometimes stated, but still from 15 to 30 per cent. From his experience, the writer would say that the average temperature of the flue gases, taken from the kiln mouth before being diluted with the air leaking into the stack, is at least 1950° F., and that the excess air is 20 per cent. of that actually required. The average coal consumed is 100 lbs. per barrel (not counting coal used to heat up kiln after patching, etc.,) and the average weight of CO_2 driven off per barrel is 200 lbs.

Then using data, in Table XVIII, the heat lost up the stack is:

		B. T. U. per degree above temp. of atmosphere.	B. T. U. in gases.
In products of combustion of 100 lbs. of coal = 100 × 10.9 × .251 = ...		273.6	
In CO^2 driven off from raw material = 200 × 0.234 = ...		46.8	
In excess air used to burn coal = 100 × 10.0 × 0.20 × 0.238		47.6	
		368.0	
If the outside air is 50° F. the gases would contain 368.0 × (1950 — 50) = ...			700,150
If raw material contains 2% moisture, to raise 600 × 0.02 or 12 lbs. of water from 50° to 212° F. requires 12 × (212 — 50) = ...	1,944		23,547
To evaporate 12 lbs. of water requires 12 × 966 = ...	11,592		
To raise 12 lbs. steam from 212 to 1950 = (1950 — 212) × 12 × 0.48.	10,011		
Total heat lost in waste gases.........			723,697

Since 1 lb. coal = 14,000 B. T. U., heat lost up stack is equivalent to 723,697 ÷ 14000 = 51.7 pounds of coal.

Also 380 lbs. of clinker at 2160° F. (usual temperature of clinker leaving the kiln) will contain 380 × (2160 — 50) × 0.246 = 197,243 B. T. U. or $\frac{197,243}{14,000}$ = 14.1 pounds of coal.

Total heat carried off by the waste gases and clinker is therefore equivalent to 65.8 pounds of coal or 65.8 per cent. of fuel.

The above conditions are not exaggerated, but are a fair example of conditions as they are usually met with in burning dry material.

It is interesting to note to what figure ideal practice would reduce the coal consumption. If the kiln gases are reduced to 450° F., it will be no better than ordinary boiler practice in many power plants. The excess air is now as low as 20 per cent. It would also be possible to reduce the temperature of the clinker to 150° F., or even lower. Under these conditions let $X =$ coal consumed:

Then as before heat carried off:

	B. T. U. per degree above temperature of atmosphere
In products of combustion $X \times 10.9 \times 0.251 =$	$2.74X$
In CO_2 from raw material..........................	46.8
In excess air $X \times 10.0 \times 0.20 \times 0.238$	$0.48X$

Total $= (2.74X + 0.48\ X + 46.8)\ 400 = (3.22\ X + 46.8)\ 400 =$ ....$1288\ X + 18720$

To raise 12 lbs. water from 50-212°F and evaporate same $=$ 13536

To raise 12 lbs. steam from 212-450 $= (450 - 212) \times 12 \times 0.48$.. 1371

Total to evaporate water............... 14,907 B. T. U.

Total heat in products of combustion, $1288\ X + 18720 + 14{,}907 =$ .... $1288\ X + 33.627$ B. T. U.

Now the clinker will carry off at 150° F. $380 \times (150 - 50) \times 0.246 = 9348$ B. T. U.

The chemical reaction will require as calculated $47{,}489 \times 6 = 284{,}934$ B. T. U.

Or the whole process will require $1288\ X + 33{,}627 + 9{,}348 + 284{,}934$ B. T. U.

Or since coal gives off 14,000 B. T. U. we have the equation, $1288\ X + 33{,}627 + 9{,}348 + 284{,}934 = 14000\ X$.

Or $327{,}909 = 12{,}712X$.

$X = 25.8$ pounds.

Therefore, we should hope to burn cement ultimately with 30 lbs. of coal per barrel. Of course the value of coal depends largely upon the heat units it contains and 40 per cent. more of a coal giving off only 10,000 heat units will be required.

Excess Air Used in Burning.

The excess of air admitted to the kiln over and above that required to consume the coal has been variously stated at from

100 to 150 per cent. above the theoretical quantity. From the result of many analyses made by myself and friends I am confident that this does not represent normal conditions. If the sample is taken from the kiln stack a large quantity of air, which has leaked in through the annular opening between the kiln and the brickwork of the flue is sure to be present, and consequently make the excess air appear much greater than it really is. The gas samples should be taken from inside the mouth of the kiln so that there is no air mixed with it which does not pass through the kiln. Below are given some average analyses of waste gases from kilns working under various conditions.

1. Average of all samples taken when the kiln was working normally. No flame or black smoke issuing from the kiln stack but only a thin white or reddish vapor.

Carbon Dioxide	27.4
Carbon Monoxide	0.3
Oxygen	2.7
Nitrogen	69.6
	100.0

2. Average of all samples taken when the kiln stacks were smoking.

Carbon Dioxide	19.2
Carbon Monoxide	1.2
Oxygen	3.4
Nitrogen	76.2
	100.0

3. Average of all samples taken when kiln stacks were flaming:

Carbon Dioxide	14.2
Carbon Monoxide	5.8
Oxygen	1.1
Nitrogen	78.9
	100.0

The nitrogen in the gases represents the air admitted for combustion as practically all of it is from either the excess air or the air actually used to burn the coal. A small part of the nitrogen comes from the coal, however, but for practical calculations the nitrogen may be considered as all coming from the air. The excess air is shown by the oxygen. If we calculate the nitrogen equivalent to this oxygen by multiplying the percentage of the latter by 3.78, the result will be the nitrogen carried in by the excess air and this nitrogen subtracted from the total percentage of nitrogen found by the analysis will give the nitrogen belonging to the air needed to support combustion, from which data the excess can be calculated. For example, to find excess air in sample:

Analysis No. 1.

	Per cent.
Total nitrogen	69.6
Nitrogen in excess air 2.7 × 3.78	10.2
Nitrogen in necessary air	59.4

Ratio: 59.4 : 69.4 : : 100 : x

$x = 117.$

Excess $= 17\%$ of air necessary to combustion.

The above calculation is not strictly accurate for a number of reasons, but for practical use it answers the purpose as well since we never know in mill practice under present conditions exactly how much coal we are burning, or how much carbon dioxide is being driven off at a given time from the raw material.

Of the air admitted to the kiln for combustion, between 20 and 30 per cent. is blown in with the coal; the rest enters between the hood and the kiln and where the clinker drops out, and is drawn in by the draft of the kiln.

Utilization of Waste Heat.

Many ways have been proposed for saving the waste heat from the rotary kiln, both in the flue gases and the clinker.

Robert F. Wentz and Lathbury and Spackman both patented clinker cooling devices on the principle of blowing air through the clinker and using the same for combustion of the coal, and each firm has installed their system in the mills which they designed. Rotary coolers are also in use in a large number of works, but as we have said the majority of mills use the large upright coolers mentioned in the section on cooling the clinkers and no attempt is made to save the heat of the clinker in spite of the fact that the heat in the clinker represents that from the combustion of 14 lbs. of coal. There should be no mechanical trouble about designing a cooler to economize this heat, and yet cool the clinker. In some of the regenerative systems the writer believes failure to have resulted simply from the fact that the designers did not realize that one cubic foot of air at 600° F. would not burn as much coal as one cubic foot of air at 60° F., but only about half as much, and consequent use of too small a fan to draw the air through the cooler. The use of the heat of the clinker to heat the water for the boilers should also prove an easy problem.

In the early days of the rotary kiln Giron, Nivarro, Hurry and others patented devices for utilizing the heat of the waste gases.

At the present time two methods are being experimented with for the saving of the heat in the kiln gases.

(1). Lengthening the kiln, thereby giving greater time for the material to absorb the heat of the kiln gases.

(2). Passing the gases of the ordinary short kiln through an upright boiler and then through an economizer.

Thomas A. Edison is the chief exponent of the long kiln, as those in his plant at Stewartsville are 150 feet long. He was the first person in this country to attempt such a long kiln.

These kilns were put in operation in the fall of 1903 and proved entirely practical and effected the economy in fuel which Edison had promised they would do. His experiment was watched with great interest, and, as soon as the success of these mammoth kilns was known, several of the mills then under construction lengthened their kilns to 80 feet. This plan has also been tried by some of the older mills who extended their kilns to 80 or 100 feet. Several of the mills now being built are erecting 100 and 125-foot kilns.

Detailed information as to the actual economy of the long kilns is hard to secure. From my own observation and tests of the 150 foot kiln I should place their output at 750 barrels per day with a coal consumption of 85 lbs. per barrel. From the most reliable data available the 80 foot kilns on dry material should turn out 300 barrels per day with a coal consumption of 90-95 lbs., and the 100 foot kilns should turn out 400 barrels per day with a coal consumption of 85-90 lbs. per barrel. The long kiln, 100 feet, working on wet materials, has reduced the coal consumption to about 110 lbs. per barrel with an output of about 150 barrels per day. In the Great Northern Portland Cement Co. the equivalent of a kiln 120 feet in length is used, the upper 60 foot portion being for mechanical reasons separated from the lower part, and arranged so that it can receive the waste heat from the boilers and from an additional fire underneath the drier when desired. The results showed a decided increase in quantity and an improvement in economy, as compared with those usually obtained in burning materials containing the same amount of water.

Quite a number of mills working on wet materials have used similar separate driers through which the kiln gases are passed.

The output of a kiln is not only dependent upon the length but also upon the diameter. Eighty and 100 ft. kilns are usually made 7 ft. in diameter. The greater the diameter the greater the output of the kiln, but the greater also its coal consumption per barrel.

Edison's 150 foot kilns are 9 feet in diameter and each kiln consists of a series of cast iron cylindrical shells bolted together and lined with fire brick. They are driven at a point toward the center by a 25-horse-power motor with speed reduction gears meshing with a large spur gear around the kiln. The kiln is supported at an angle of 2½ degrees with the horizontal by means of thirty supporting wheels and the thrust; owing to its inclined position, it is taken up by two auxiliary wheels bearing against collars, as shown. Ordinarily the kilns are rotated at a speed of 1 turn per minute and the material in passage through it takes about 1½ hours. At the discharge end it falls into a secondary revolving cylinder which is furnished to serve as a clinker cooler and a regenerator, in that the air passed upward through the auxiliary cylinder is finally admitted into the kiln. Pulverized coal is employed, as usual, for combustion, but forced in by means of compressed air. Owing to the extreme length of the kiln, two coal jets are employed, one with air at a higher pressure than the other to throw the coal jet as great a distance as possible.

The attempt to utilize the heat of the kiln gases under boilers was first made, I believe, at the plant of the Nazareth Portland Cement Co., but after encountering many difficulties, the plan was abandoned and the boilers taken away. Prof. R. C. Carpenter, of Cornell University, however, has successfully tried this plan at the plant of the Cayuga Lake Cement Co.

The works referred to have a small plant consisting of four kilns and grinding machinery sufficient for about 600 barrels per day, which is located on the shores of Cayuga Lake, about six miles north of Ithaca, N. Y. In this plant one boiler, of the vertical water-tube type, as built by the Wickes Bros. Mfg. Co., and of 3,000 square feet of water heating surface, was installed for each two kilns of the plant. After two kilns, composing one-half of the plant, had been in operation about two months, a test was made to determine the economy of the plant and also the amount of steam obtained from the waste gases.

Prof. Carpenter[1] gives the following description of the test and its results.

At the time of the test two kilns only were in operation and the waste heat from these kilns passed through one boiler; the other boiler when used being fired by hand exclusively. The tests of the two boilers were made on different days. The test showed that boiler No. 1, which received the waste gases, developed 406.8 B. H. P., of which it was calculated that 264 B. H. P. was produced by the waste heat from the two kilns and the remainder from coal burned on the grate. When boiler No. 2 was tested, boiler No. 1 received the heat from the waste gases of two kilns and no heat from hand firing, and during this time a measurement of the feed water indicated that the heat from the waste gases was sufficient to produce 254 B. H. P., which roughly checks the preceding test.

Practically all cement manufacturers realize the great loss of heat due to the high temperature of the kiln gases, and it is only a question of time until all plants will have adopted some method of saving this waste heat. The long kiln seems to be the favorite method at present adopted by the newer mills, and many of the old ones are lengthening their kilns to from 100 to 120 feet. While the long kiln will effect some economy the 80 and 100-foot kilns will still be quite wasteful, for if the 60-foot kiln only absorbs 20 or 30 per cent. of the heat of combustion, it would seem as if

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[1] Sibley *Journal of Engineering*, March, 1904; also Concrete, November, 1904.

Prof. Carpenter's plan of utilizing the kiln gases in a boiler would really effect the greater economy. The difficulty that has kept the cement manufacturer from making use of the hot blast stoves of the iron manufacturer, namely, the large quantity of dust in the kiln gases, has also interfered somewhat with the previous attempts to use the waste gases under boilers, but I believe Prof. Carpenter claims to have eliminated this trouble.

From some observations made on the flue gases of the 150-foot kilns I am confident that in order to reduce the kiln gases to 400° F the temperature obtained in good boiler practice, it would be necessary to lengthen these kilns to at least 250 feet. In this connection it may be said that the diameter of the kiln will have some effect on the economy. The smaller the diameter for a given length the greater the economy. To decrease the diameter however, is to decrease the capacity because it decreases the coal which can be burned.

CHAPTER VIII.

COOLING AND GRINDING THE CLINKER, STORING AND PACKING THE CEMEMT, ETC.

Cooling the Clinker.

The clinker leaves the kiln at a temperature of about 2100° F. It is, of course, entirely too hot to grind and must be cooled. It has generally been found preferable to do this mechanically instead of letting the clinker lie in heaps and cool of itself. In some mills this has been done in pits, in others in rotary coolers, but the majority of the mills use the upright cooler shown in Fig. 33. This consists of an upright steel cylinder about 8 feet in diameter and 35 feet high provided as shown with baffle plates and shelves. As the clinker falls over these it meets a current of air blown in through a perforated pipe running up through the centre of the cylinder and is thus cooled. There is usually one cooler to each pair of kilns. The clinker is lead from these latter by chutes to a common bucket elevator which carries it to the top of the cooler. Usually water is added to the clinker in a steady stream as it falls into the elevator pit. This helps to cool the clinker, makes it more brittle and easier to grind in the ball mill and saves the elevator from handling such very hot material. There is probably nothing in the curing of the cement or the hydration of the free lime, since any of the former present is usually locked up in the interior of the clinker. It may, however, prevent the crystallization of the more soluble di-calcium aluminate from the magma of the clinker and so help the quality of the cement. The writer has frequently cooled clinker suddenly by plunging it, red hot from the mouth of the kilns, into water. The only perceptible effect is to bleach the color from dark greenish black to nearly white. If this clinker is dried and ground, it will be found to have pretty much the same properties as clinker caught at the same time and allowed to cool slowly in air. The writer has never observed that unsound cement could be made sound by this process. It does take up some water (probably on the outside of the lumps only, however), as a loss on ignition test will show. Such clinker is easily ground and the resulting cement trowels nicely. This greenish white color of water cooled clinker is probably the normal color of the cement clinker *when hot,* as in this state all compounds are in solution in the fusible magma of the clinker. On cooling slowly the iron

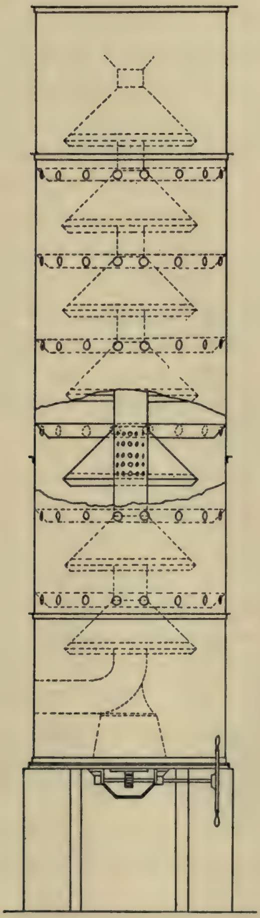

Fig. 33. Upright Clinker Cooler (Mosser & Son.)

separates out as black magnetic oxide of iron, Fe_3O_4, but on suddenly cooling it does not have time to do this.

The clinker is usually drawn from the bottom of the cooler on to belt conveyors, or else into barrows and carried to an elevator, which carries it up to the bins above the ball mills or rolls, which ever are used to grind the clinker.

Some mills use a rotary cooler which consists of a steel shell similar to that of the kiln and mounted on friction rollers just as the kiln is. Usually this is lined with fire brick. One cooler is used for two kilns and air is blown up through the cylinder to cool the clinker. Such coolers act as pre-heaters to the air entering the kiln. A form of cooler used by one of the New York State mills recently came to the writer's notice. It consisted of a water jacketed revolving cooler. The water entering and leaving the jacket through pipes leading from a specially designed feeder placed in the centre of the discharge end of the cooler. The water after leaving the cooler was used in the boilers, the cooler simply acting as a preheater. These coolers are said to have worked well, and to have cooled the clinker perfectly.

Cooling clinker in pits has been tried at a number of places, but does not seem to have worked very well anywhere. Some few mills convey their clinker red hot out into the fields and allow it to cool naturally. Such clinker is easily ground and has usually absorbed some moisture so that for every 100 barrels of clinker burned the manufacturer should grind from 101 to 104 barrels. A sort of case of watered stock, except that in this case the water probably does some good. The great difficulty with this system of storage is the conveying of the red hot clinkers out into the fields. Getting them back to the mill is, of course, easy as any of the coal handling devices, such as ærial cables and orange peel buckets, which will do this satisfactorily, or tunnels provided with belt conveyors under the piles may be used.

Grinding the Clinker.

The clinker is ground in Griffin mills or ball and tube mills, all of which have been described in the section on grinding the raw materials. At the mills of the Atlas Portland Cement Co. the clinker is ground in Huntington mills and at one or two mills the

Kent mill is being used for this purpose. It is usual for the clinker to be ground by the same type of machinery as is used to grind the raw material. The principal reason for this is that only one set of repair parts have to be carried in stock. A number of mills, however, use ball and tube mills to grind the raw materials and Griffin mills to grind the clinker, the idea being that the former is the better of the two for soft materials, and the latter the more suited to the hard clinker. The tube mill is also a splendid mixer for hard and soft materials, such as clay and limestone. The tube mill is also well suited to wet grinding, and hence to marl and clay.

Kent Mill.

This is a new mill which has so far been used in connection with some form of separator, both to prepare material for the tube mill and also to do the final grinding. This mill, the principle of which is illustrated in Fig. 34, consists of a vertical revolving ring, having three grinding rolls which are mounted on horizontal shafts and which press against the inner surface of the ring. The material to be ground is fed on the inner surface of the ring and is ground between this and the rolls. The inner surface of the ring is slightly concave and the cement is kept in

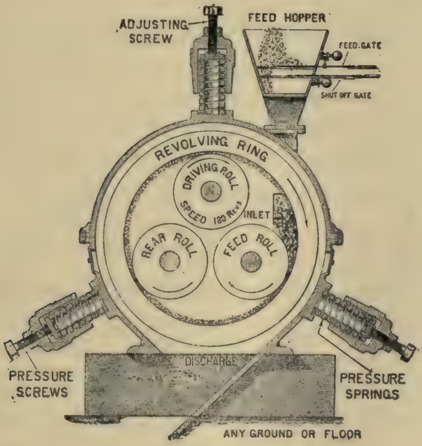

Fig. 34. Kent Mill.

the center of this and between the ring and rolls by centrifugal force.

The Kent mill requires the use of an outside separator; that is, the material as delivered by the mill itself consists of both coarse and fine particles, and the latter must be separated from the mixture, and the former returned to the mill for further grinding. At the plant of the Newago Portland Cement Co., where the Kent mill is used, a shaking screen of wire cloth has been devised for this purpose, but the majority of the manufacturers who are experimenting with the Kent mill are using the Emerick separator or the Pfeiffer separator. Both these machines are similar in principle, and make use of a current of air to separate the fine from the coarse particles.

Air Separators.

The Pfeiffer separator is much used in Germany and Europe to take out the fine material from the product of the ball mill, and so relieve the tube mill of some of its work. The separator is shown (in section) in Fig. 35. It consists of an outer and an inner cone of sheet metal as shown in the drawing. The material to be separated is fed into the mill through the hopper on to a plate, which is connected to a vertical shaft, and is revolved at a speed of about 200 revolutions per minute. The material is thrown off this plate in a thin spray, by centrifugal force, and is met by a current of air, going in the direction shown by the arrows. The coarse particles fall through this current into the inner case, and the finer ones are carried into the outer space, between the inner and outer cones. The air currents are maintained by the fans as shown.

At the plant of the Hudson Cement Co. the separators are used after the tube mills. The grit passes directly from the ball mills through the tube mills and from the latter to the separators. The fine material is sent from the separators to the stock house, and coarse particles are returned to the tube mill. The separators increased the capacity of the tube mills from 8 barrels per hour, of a fineness of from 93 to 94 per cent. through a No. 100 sieve, to 13 to 15 barrels per hour, of a fineness of 96-98 per cent. through a No. 100 sieve.

At one of the mills of the Lehigh District, a Kent mill working

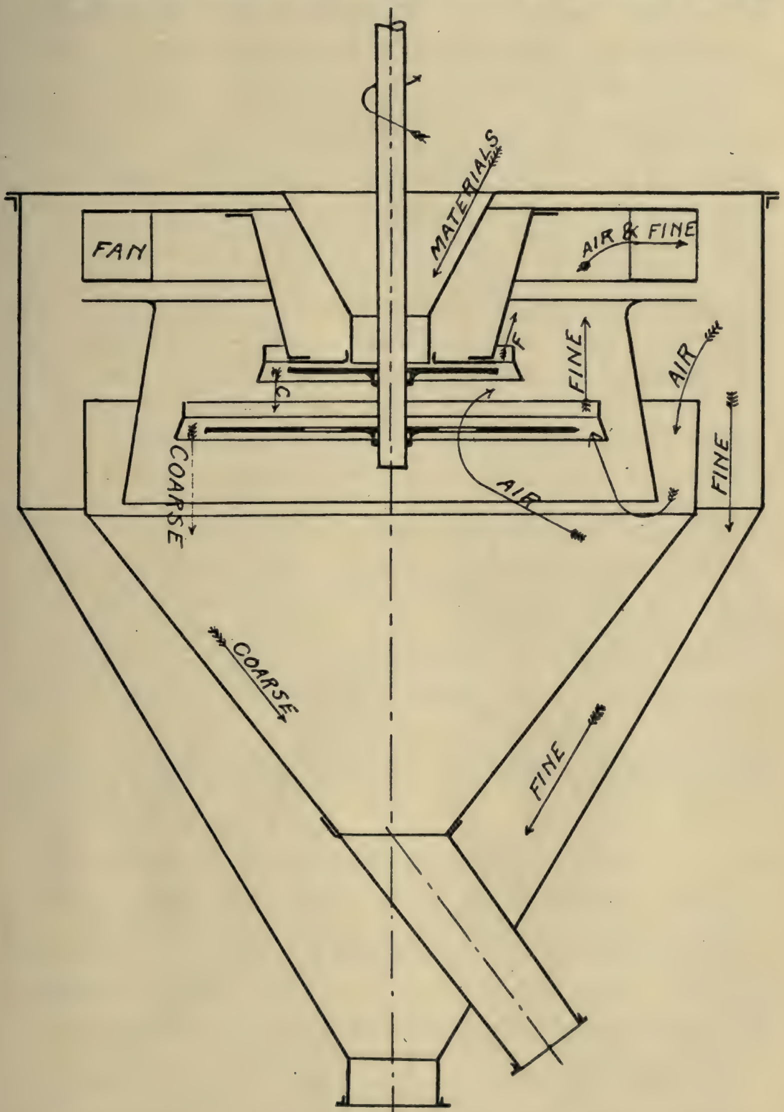

Fig. 35. Pfeiffer Air Separator.

in combination with a Pfeiffer separator ground 11 barrels of cement per hour with an expenditure of about 30 horse-power for the mill, separator and attendant elevators and conveyors. The mill itself requires about 25 horse-power and the separator from 1 to 2 horse-power.

As has been said the use of separators to take out the fine particles from the ball mill product and so relieve the tube mill of part of its work is quite general in Germany, but so far has not been tried to any extent in this country. A ball mill provided with 16-mesh screens of No. 23 wire will give a product containing between 15 and 20 per cent. of material passing a No. 200 test screen. The Kominuter on the other hand gives a much larger percentage of fine material, as would be supposed since the material must travel from end to end of the drum before passing out, while in the ball mill it falls through the plates and screens as soon as ground. A test of the Kominuter product made by the writer gave 25 per cent. passing through a No. 200 sieve and 40 per cent. through a No. 100 sieve. In this case the screens were 16 mesh and of No. 23 wire. A finer mesh screen on either ball mill or Kominuter will, of course, give a product containing more fine material. This fine material from the Kominuter contains considerable flour as sand briquettes made of the material passing a No. 200 sieve gave 335 lbs. for 7 days and 447 lbs. for 28 days. The material passing the No. 100 sieve gave 267 lbs. for 7 days and 320 lbs. for 28 days.

The Emerick separator is similar in principle to the Pfeiffer, but differs from it somewhat in construction. It has been tried with marked success by one plant in the Lehigh Valley. In this mill the addition of a 9-foot Emerick separator after the mill increased the output of one of their tube mills from 9 barrels of cement per hour to 18 barrels per hour—grinding in both cases to the same fineness, 75% through a No. 200 sieve. Part of this increased output was, however, due to more efficient working of the tube mill itself. In the same mill a 10 foot separator increased the output of a tube mill from 11 barrels per hour to 24 barrels per hour. The entire grinding plant of the Buckhorn Portland Cement Co. is equipped with these separators, and they are being given a trial by American cement manufacturers generally, about

50 of them having been placed in the different mills during the past six months.

A rather amusing discussion[1] of the separator question appeared in one of the engineering magazines, about a year ago, in which the author took the ground that the separators destroy the uniformity of the product and that for example in a clay-limestone mixture the lighter particles of clay would be blown away from the heavier limestone. The author seems to have overlooked the fact that by pulverizing the limestone particles a little finer they too will be blown out by fans of the separator so that while it may be true that on starting up a new separator the first product will be slightly over-clayed, the trouble will be adjusted by the return of the limestone to the grinder for finer pulverizing, after which it will be blown out on its next passage through the separator *together with the clay from the new lot of mix fed into the tube mill,* the process being a continuous one. This same objection can be raised against ball mills that the softer particles of clay or cement rock will be pulverized sooner and drop through the screens of the ball mill before the limestone. In this case also this irregularity adjusts itself and in the same manner. My own personal experience with air separation at the plant of the Edison Portland Cement Co. convinces me that there is nothing against its use on the ground of lack of uniformity in the product. In the Griffin mill the separation of the finer from the coarser particles is effected by air separation, as the fans placed on the shaft blow the fine material through the screen.

Stock Houses.

From the grinding mills the finished cement goes to the stock house. This usually consists of a long low frame building divided into bins, by means of wooden partitions, so that each day's grinding may be kept separate. These bins usually hold from 1000-2000 barrels and are arranged either on each side of a central aisle or else with an aisle on each side. The parts of the bins facing the aisles are stopped up by means of boards which may be easily removed, and below the floor of the aisles, run

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[1] "Some of the Reasons Why Separators are not Used in Portland Cement Works." E. C. Eckel, *Engineering News*, Vol. LI., p. 344.

screw conveyors to the packing room, which is usually one end or a large room in the middle of the stock house. The screw conveyors are covered with boards, except in front of the bins where gratings three of four feet in length are placed. The cement is usually brought in from the grinding mills by an overhead screw conveyor, from the trough of which spouts run to the middle of the bins. The openings in the trough leading into the spouts are closed by iron slides or gates so that the cement may be run into any bin desired at any time. When it is desired to open a bin the bottom plank is removed from the front of the bin and the cement is allowed to run into the screw conveyor, through the grating. When it ceases to run of itself, a scraper, which consists of a flat iron plate about 6″ × 18″ from the middle of which a long handle projects, is introduced and all of the cement which can be pulled through the opening conveniently is drawn into the conveyor, after which the remainder of the boards are taken down, and the rest of the cement is drawn into the conveyor, either with the scraper or wheeled by barrows to the grating. To do away with the manual labor required by such a method of opening a bin, stock houses provided with tunnels running under the bins are used. The conveyors are located in the tunnel and the bins are fixed with sloping floors and spouts, which deliver into the conveyor. A simpler method and one which is adapted to the improvement of old stock houses is to put in small conveyors running across the bins and emptying into the main conveyors. The stock-house of the Illinois Steel Co.,[1] consists of four cylindrical Monier concrete steel bins in a group. The bins are 25 feet in diameter and 53 feet high and hold about 7,500 barrels each. The cement is tapped out below.

Packing.

Cement is packed into wooden barrels holding 380 lbs. or into paper or cloth bags holding 95 lbs. by means of packers, such as are used for packing flour. The cement is packed as shipped and the bags or barrels are trucked directly to the cars. For this reason the packing room should be so arranged that the cars to be loaded can be brought alongside of the room and a shed roof

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[1] *Cement*, III, 4, 286; *Cement and Engineering News*, 1903, p. 55.

should be run out over the cars so the loading will not be interrupted by rainy weather. Since some seasons of the year are much busier than others, the packing house should be able to load and ship at least twice as much cement as the mill can make in a day. The floor of the packing room should be on a level with the floor of the cars to be loaded. Cloth bags are used much more for packing cement than anything else. In the case of cloth bags the consumer is charged with the value of the bag, 10 cents, and credited by 7½ cents when the bag is returned. The bags are all marked with the label of the brand and so each manufacturer knows his own bags. Barrels and paper bags are sold to the customer and are not returnable.

Nearly all cement mills have a cooper shop connected with the mill. Some of these shops are equipped with barrel making machinery, and at others all the work is done by hand.

Power Plant.

The grinding proposition of a modern cement mill is one of considerable magnitude. A 1000 barrel a day plant must grind about 500 tons of material to an almost impalpable powder every twenty-four hours. Three hundred tons of this represent the raw material which must be reduced from pieces of stone as large as a man can handle to such a degree of fineness that from 90 to 98 per cent. of the powder will pass a 100-mesh test sieve. The other 200 tons represents the slag like clinker which must be pulverized so fine that at least 92 per cent. of it will pass this sieve. The power required to run the amount of machinery necessary to grind this quantity of material is probably greater than that which would be utilized in the manufacture of a similar value of any other commodity.

The size of the power plant which will be required in manufacturing 1000 barrels of cement per day will depend largely upon the class of material to be ground, upon the type of machinery used to do this, the thoroughness with which it is done, as well as the proper installation of the plant itself and the means of transmitting the power to the machinery. The cheapness with which cement can be manufactured will hinge largely on these points and hence the power plant of an up-to-date cement mill must be "dead right" and embody the most economic devices for the production and use of steam. The boilers must be of the most improved type and the engines of the most modern pattern. The latter must be heavily made and able to stand continual heavy duty. The general character of the power generators themselves and the arrangement of the engine and boiler rooms is similar to that of other manufacturing enterprises where much slow moving heavy machinery is employed. Not only must the engines and boilers be of the proper type, but the distribution of the power to the mills must be effected with the least possible loss due to friction. To this end short powerful shafts are used which are driven by belting or rope drivers, directly from the engines, and which transmit the power to crushers, and grinding mills. In some mills the engines are connected direct or by belting to powerful electric generators and the current from these is carried about the mills by copper cables and distributed to motors which are directly connected by gearing to the mills. Where water power is at hand the generators have been connected to powerful turbines and power thus very cheaply obtained. It is also proposed to utilize the power in the waste gases from blast furnaces for cement manufacture. At the new plant of the Illinois Steel Co., at Buffington, Ind., the waste energy in the gases from the iron furnaces of this company at Joliet, Illinois, is to be converted into electrical power and transmitted some eight miles over the Chicago River to the cement plant.

In designing the power plant of a cement mill, it has usually been found best to run the mills grinding raw material with one engine and those grinding clinker by another, rather than to use one large engine for both. It has also been found best to run the kilns by a separate engine so that shut downs may be avoided.

The actual power which will be required by any cement mill, as we have said before, will depend entirely upon circumstances. To operate a mill making 1000 barrels of cement from cement rock and limestone will require at least 1000 horse-power. A mill of this size, working on marl and clay, will require a little less, while one on clay and limestone will require a little more. In

general, it may be said that it will require from 0.8 to 1.2 horsepower for each barrel per day capacity of the mill to operate the machinery. Faulty installation and very hard raw materials may easily run this figure up to 1.5 horse-power per barrel of cement per day capacity. Roughly speaking, about two-thirds of this power will be required to run the grinding mills; and on dry materials of average hardness, such as limestone and cement rock, this will be about evenly distributed between the two grinding departments.

Complete Equipment of Plants.

Fig. 36 shows the arrangement of the machinery and the distribution of power, etc., in a modern wet process plant; while Fig. 37 shows that of a dry process mill. In the latter all the machinery is driven by motors directly connected to the mills by gearing.

Table XIX which follows shows the mechanical equipment of eight modern Portland cement plants.

References to Descriptions of Plants.

More or less detailed descriptions of the following plants will be found in the books and journals indicated. The plants marked with an asterisk (*) are wet process plants.

Alma Portland Cement Co., Wellston, O. The Rotary Kiln[1], p. 44.

Alpha Portland Cement Co., Alpha, N. J. Engineering News, Vol. XLIV, p. 313.

Alsen's American Portland Cement Works, West Camp, N. Y. The Rotary Kiln, p. 52; Engineering Record, Vol. XLVII, p. 10.

American Cement Co., Egypt, Pa. The Rotary Kiln, p. 66.

Atlas Portland Cement Co. Proc. Inst. of Civil Eng. (British), Vol. CXLV, p. 57.

*Beaver Portland Cement Co., Marlbank, Canada. The Rotary Kiln, p. 74; Cement and Engineering News, VIII, p. 72.

*Bronson Portland Cement Co., Bronson, Mich. The Cement Industry[2], p. 33. Engineering Record, April 30, 1898.

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[1] The Rotary Kiln. 206 Pages. Price, $2.00. Lathbury & Spackman, Philadelphia 1902.

[2] The Cement Industry. 235 pages. Price, $3.00. McGraw Pub. Co., New York.

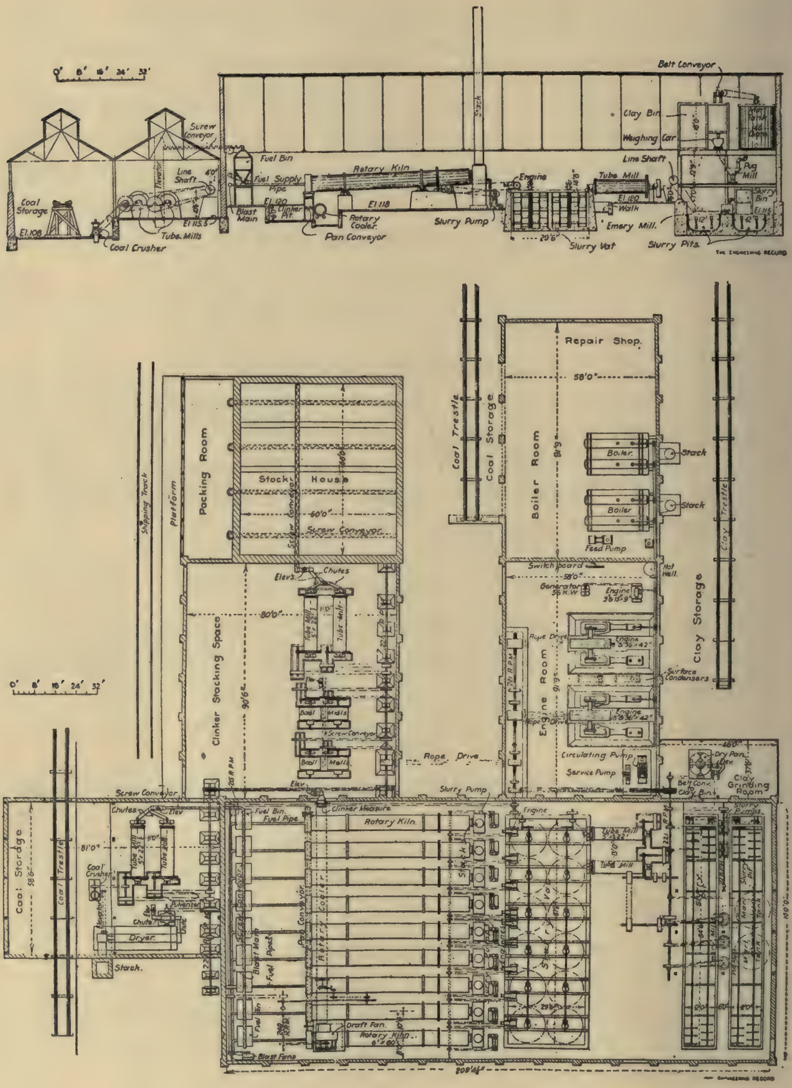

Fig. 36. Plan and Section of the Egyptian Portland Cement Co.'s Works at Fenion, Mich. (Engineering Record.)

*Buckeye Portland Cement Co., near Bellefontaine, O. The Cement Industry, p. 52; Engineering Record, October 15, 1898.

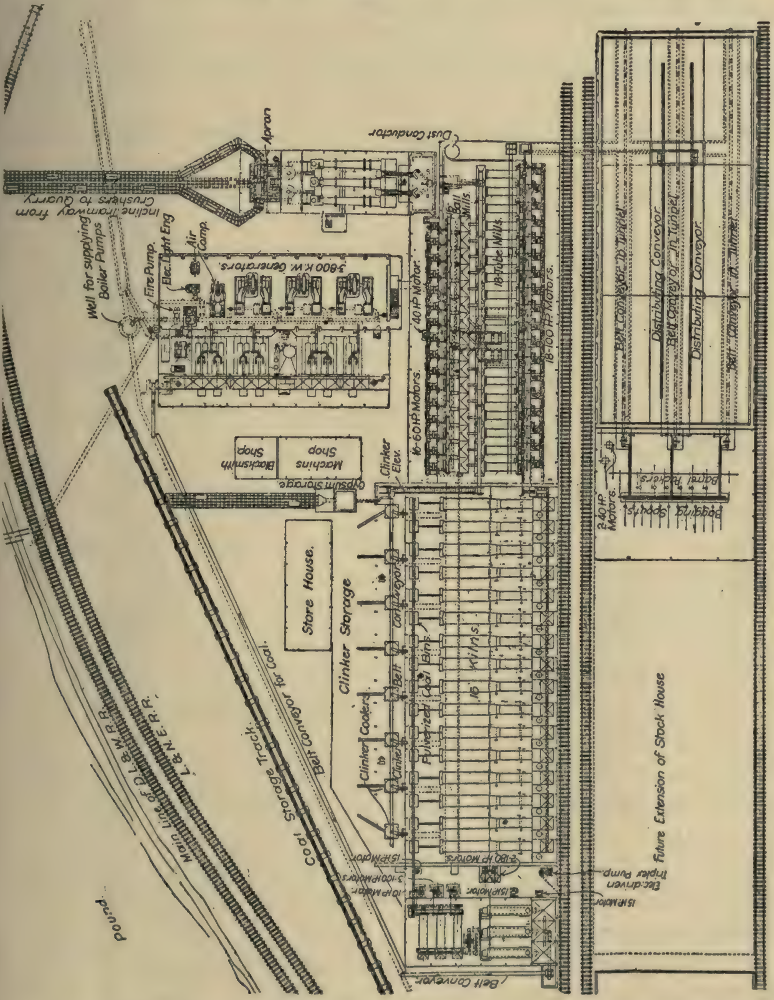

Fig. 37. Plan of the National Portland Cement Co.'s Works, at Martins Creek, Pa. (Engineering Record.)

Buckhorn Portland Cement Co., Manheim, W. Va. Engineering News, Vol. L, p. 408.

*Castalia Portland Cement Co., Castalia, O. The Rotary Kiln, p. 78.

[1]Clinton Cement Co., Pittsburg, Pa. The Rotary Kiln, p. 82.

Colorado Portland Cement Co., Portland, Colo. Engineering Record, Vol. XLIX, p. 223 and 242.

Coplay Cement Co., Coplay, Pa. The Cement Industry, p. 20 and 69. Engineering Record, December 18, 1897; and February 27, 1900.

*Detroit Portland Cement Co., Fenton, Mich. The Rotary Kiln, p. 86.

Dexter Portland Cement Co., Nazareth, Pa. Engineering Record, Vol. L, 160.

Edison Portland Cement Co., near Stewartsville, N. J. Engineering Record, Vol. XLVIII, p. 796; Engineering News, Vol. L, 555; Cement and Engineering News, Vol. XV, p. 137.

*Egyptian Portland Cement Co., near Fenton, Mich. Engineering Record, Vol. XLIX, p. 320.

*Empire Portland Cement Co., Warners, N. Y. Cement Industry, p. 45. Engineering Record, July 16, 1898.

Hudson Portland Cement Co., Hudson, N. Y. Engineering News, Vol. L, p. 70.

*Hecla Portland Cement Co., Bay City, Mich. Engineering News, Vol. LI, p. 243.

*International Portland Cement Co., Hull, P. O., Canada. Engineering Record, Vol. LI, p. 106; Cement and Engineering News, Vol. XVII, p. 72.

Iola Portland Cement Co., Iola, Kans. Engineering and Mining Journal, February 16, 1901.

Kosmos Portland Cement Co., Kosmosdale, Ky. Cement and Engineering News, Vol. XVII, p. 30; Engineering Record, Vol. LII, p. 459.

Lawrence Cement Co. of Pennsylvania, Siegfried, Pa. The Rotary Kiln, p. 96. The Cement Industry, p. 117. Engineering Record, May 12, 1900.

Martin's Creek Portland Cement Co., Martin's Creek, Pa. The Cement Industry, p. 107. Engineering Record, March 31, 1901.

[2]Michigan Alkali Co., (now Wyandotte Portland Cement Co.), Wyandotte, Mich. The Rotary Kiln, p. 110; Engineering News, June 7, 1900.

[1] Manufactures Portland Cement from slag and limestone.

[2] Designed to use alkali waste and clay. Now uses limestone and clay.

*Michigan Portland Cement Co., Coldwater, Mich. The Cement Industry, p. 78. Engineering Record, February 25, 1899.

National Portland Cement Co., Martin's Creek, Pa. Engineering Record, Vol. LI, p. 288 and 316.

Nazareth Portland Cement Co., Nazareth, Pa. The Cement Industry, p. 85. Engineering Record, December 16, 1899.

Northampton Portland Cement Co., Stockertown, Pa. Engineering Record, Vol. XLVIII, p. 182.

Pembina Portland Cement Co., Milton, N. D. The Rotary Kiln, p. 124.

Portland Cement Co., of Utah, Salt Lake City, U. The Rotary Kiln, p. 127.

St. Louis Portland Cement Co., Prospect Hill, Mo. Engineering Record, Vol. XLVIII, p. 36.

Virginia Portland Cement Co., Fordwick, Va. The Cement Industry, p. 132; Engineering Record, July 28, 1900.

Vulcanite Portland Cement Co., near Phillipsburg, N. J. Cement Industry, p. 96. Engineering Record, May 6, 1899.

*Wabash Portland Cement Co., Stroh, Ind. The Rotary Kiln, p. 128.

*Western Portland Cement Co., Yankton, S. D. The Cement Industry, p. 60. Engineering Record, November 19, 1898.

Whitehall Portland Cement Co., Cementon, Pa. The Cement Industry, p. 142. Engineering Record, September 15, 1900. Cement and Engineering News, Vol. IX, p. 23.

Cost of Plant and Manufacture.

A great many itemized statements, showing the cost of erecting a Portland cement plant and of manufacturing a barrel of cement, have been published in the last few years—no two of them agreeing and probably none of them coming anywhere near the truth. For instance, in one widely quoted estimate, showing the average cost of making a barrel of Portland cement at an ideal 2000 barrel plant in the Lehigh District, the estimator has assumed that 5 barrels of cement can be made from one ton of rock; whereas, a tyro chemist knows that the plant is doing well which gets 3.3 barrels from a ton of raw material. Very few engineers in their estimates of the cost of making a barrel of cement have included depreciation of buildings and the actual value of raw material used. This latter item is an important one, in spite of its being overlooked. For example, suppose a mill using marl and clay has available a supply of marl sufficient for the manufacture of 3,000,000 barrels of cement, and cost to erect, buy the land and put in operation $300,000. Then 10 cents at least should be added to the mill cost of making a barrel of cement, because the stockholders will have nothing for their original expenditure (except second-hand machinery) when they will have made their 3,000,000 barrels, and hence it will have cost them 10 cents a barrel more than the actual mill expenditure to make that quantity of cement.

Similarly, much has been written as to the cost of building cement plants and these estimates are usually very much like those of cost and leave out some important items. For instance, in one estimate recently published in a bulletin of one of the state geological surveys, the machinery is probably assumed to run itself, since no figures are given for a power plant. Even experienced cement engineers often come very wide of the mark in their estimates of the cost of erecting plants, and it is no uncommon thing to see companies run through a liberal estimate of cash before their plant is near completion. Often, too, plants are turned over to their owners by the engineers erecting them, only for the former to find $50,000 to $100,000 must be spent, in order to make the changes necessary to a successful, economical operation of the mill. Plants trying new machinery, or working with new materials, can usually count on doing a good deal of altering on starting up; and plants designed and built by engineers inexperienced in the cement industry can feel reasonably sure, that the practical man who finally comes to their rescue will ask for a very considerable sum of money to put them on an economical working basis.

I do not believe any new plants will be built having kilns shorter than 100 feet, and I do not believe that plants smaller than 1200 to 1600 barrels capacity can be made to operate economically in the future. A plant of three 100-foot kilns will cost from $350,000 to $450,000, exclusive of the cost of the property and one of six 100-foot kilns can probably be built for from $600,000 to $750,000. These estimates are of course very general. They imply money well spent, with no wasting, and for good machinery.

Of the special machinery used in a cement plant the table below gives the approximate price.

To this must be added the cost of foundations and erection, shafting, belting, etc., to run, etc., etc.

Kiln (6′ x 60′)	$3,000.00
Fire brick Lining	300.00
Kiln (7′ x 100′)	5,000.00
Fire brick lining	600.00
Kominuter	4,500.00
Ball Mill No. 7	2,800.00
Ball Mill No. 8	3,500.00
Tube Mill (5′6″ x 22′)	3,000.00
Tube Mill (5′ x 22′)	2,500.00
Griffin Mill (30″)	2,000.00
Rock dryer	2,500.00
Coal Dryer with brickwork	3,000.00
Gates Crusher No. 5	1,700.00
Gates Crusher No. 6	2,000.00
Upright Coolers	2,000.00
Steel Storage Bins for Mills or Kilns	600.00
Coal Bins with burning apparatus	800.00
Elevators, each	450 to 600.00

The elements entering into the cost of manufacturing a barrel of cement are as follows:

(1) Labor.
(2) Supplies.
    (a) Coal for burning.
    (b) Coal for power.
    (c) Gypsum.
    (d) Limestone or clay.
    (e) Repair parts.
    (f) Lubricants.
    (g) Miscellaneous.
(3) Administrative.
    (a) Mill office.
    (b) General office.
    (c) Laboratory.
(4) Fixed charges.
    (a) Interest on Bonds, if any.
    (b) Value of raw materials used.
    (c) Insurance and taxes.
    (d) Depreciation of mill buildings and machinery.

The cost of labor varies very greatly in different sections of the country. The cost of unskilled labor can of course be estimated fairly well by any one familiar with the local conditions. In general it may be said that a 1200 to 1600 barrel mill will require one unskilled laborer for every 12 to 18 barrels of cement produced. Of the skilled laborers there will be needed a quarry foreman, drillers, millers, burners, engineers, firemen, packers, mill foremen, machinists on repair work, blacksmiths, etc. Of these the millers, burners, packers, mill foremen and some of the machinists must be experienced in cement mill work, and consequently a new mill, located in a new section must import these men from one of the old established centres of the industry and in order to induce these men to leave their homes must pay them much higher wages than the older mills do. In the east the usual charge for all labor (skilled about $2.50-$3.00. Unskilled, $1.10-$1.50) is between 15 and 20 cents per barrel.

Of the supplies, coal, gypsum and limestone (or clay) can of course be calculated fairly closely. Under favorable conditions, such as soft raw material and a well installed power generation and transmission system, a barrel of cement can be made with 60 lbs. of coal; and even hard raw materials should not increase this to more than 75 lbs. Poor engines and boilers and faulty power transmission, however, may easily raise this much higher. For the amount of coal used to burn see the chapter on burning.

Each barrel of Portland cement has added to it from 8 to 12 lbs. of gypsum. The latter is the limit placed by the standard specifications and the former is the usual amount used. If plaster of Paris is used in place of gypsum practically the same amount is required and its cost delivered is usually about twice as great.

The cost of lubricants varies greatly, but under good management and careful attention to avoid waste, can be reduced to from 0.7 to 1 cent per barrel.

The repair parts form one of the heaviest of the supply items of a cement mill and depend of course largely on the type of machinery installed to do the grinding. The Griffin mill probably costing more to keep in repairs than tube mills. The care with which the machinery is used also has a large influence on this item. Repair parts may cost anywhere from 6 to 10 cents a barrel, even with good management.

The miscellaneous supplies usually foot up to about 1 to 2 cents a barrel—dynamite forming one of the heaviest items of this. Theoretically, the container in which cement is shipped is supposed to pay for itself and is not included in the cost of mill supplies. The labor of packing has been included under labor.

The administration expenses vary greatly with the size of the mill, and the calibre of the men employed. With a small mill employing a first-class manager and chemist and good assistants, this may figure as high as 6 cents a barrel, while a large mill may reduce this easily to 2 or 3 cents a barrel.

Of the fixed charges, taxes and insurance usually amount to 1 to 2 cents a barrel. The depreciation of mill buildings and machinery are usually figured at 10% of their cost erected, and the interest on bonds, etc., can of course be calculated with certainty. To calculate the value of the raw materials used, it is necessary to know the amount of these available, when the calculation becomes merely one for arithmetic.

The cost of manufacturing Portland cement may therefore be said to depend on (1) the location of the mill and the ease with which it can obtain its supplies, (2) the cost of labor, (3) the efficiency of the machinery installed, (4) the extent, suitability and softness of the raw materials, and (5) the management and running of the mill, and the purchasing of its supplies.

ANALYTICAL METHODS.

CHAPTER IX.

THE ANALYSIS OF CEMENT.

SAMPLING.

The knowledge usually sought by a chemical analysis of cement is the average composition of a given lot or bin. In order that it shall give this, it is necessary that the small sample used in the analysis shall fairly represent the whole quantity, possibly many tons. In a large lot of cement, it is hardly probable that a small sample, or even a large sample, taken from one place in the bin or barrel in the consignment, will have the average composition of the cement, since this particular point in the bin, or this special barrel, might be better or worse than the remainder. It is well in sampling from a bin, to take small samples from various points, not merely upon the surface where the cement may have become slightly altered by exposure to air or damp, but also underneath by using a fairly long brass tube, or some other form of sampler, such as will be described hereafter.

In sampling shipments it is best to take a sample from ten or more bags or barrels in each one hundred barrels. Cement[1] in barrels should be sampled through a hole made in the centre of one of the staves, midway between the heads, or in the head, by means of an auger or sampling iron, similar to that used by sugar inspectors. If in bags it should be taken from surface to center. The sample is then usually placed in a clean paper bag or a tin bucket, labeled, and carried to the laboratory. Here the sample is well mixed by passing several times through a coarse sieve, and by rolling back and forth on a sheet of paper, or better still, one of oil cloth. When thoroughly well mixed it is spread out in a thin layer on the paper, or oil cloth, and divided into 20 to 30 little squares with the points of a spatula or trowel. A small quantity (about 2 or 3 grams) of cement is now taken from each

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[1] Committee on Uniform Tests, Am. Soc. C. E.

one of these squares with the trowel or spatula point and these small samples are mixed and ground for the chemical analysis. The main portion of the cement is then replaced in the bag or bucket and used for the physical tests.

In order that the solvents used to decompose the cement for analysis may do their work, the portion weighed out must contain no coarse pieces of clinker. To guard against this, pass the smaller sample through a No. 100-mesh test sieve, grinding any residue caught upon the sieve in an agate mortar until it, too, passes. From the size and shape of the ordinary agate mortar and pestle the operation of grinding is very fatiguing. It may be much facilitated, however, by cutting a hole, of such size and shape as to hold the mortar firmly, in the middle of a block of hard wood, a foot or so square. The pestle is then fixed in a piece of round brass tubing of sufficient bore, or else in a round hard wood handle. Several mechanical grinders are on the market, descriptions of which may be found in the trade catalogues of most of the prominent dealers in chemical apparatus.

After being ground the sample for chemical analysis should be placed in a small (one or two ounce) wide mouth bottle and tightly corked. If for immediate use a sample or coin envelope may be substituted for the bottle. The bottles are cheap enough, however, and, as cement rapidly absorbs water and carbon dioxide from the air, it is a good rule to use them altogether.

Samplers.

In sampling cement from a bag or barrel a small brass tube with a slit cut down the middle may be used. The slit is necessary as the cement becomes packed in the tube when it is thrust into the cement and it is necessary to run a lead pencil or nail up and down the opening to get the cement out. The tube for this purpose need not be over two feet long and its upper end should be screwed into a T, the latter forming a handle. The forms of grain and sugar samplers sold by dealers in apparatus for cement testing may be used also for sampling bags and barrels.

For sampling bins of cement in the stock houses at the mill the depth of the former, often eight or more feet, makes their proper sampling a difficult matter unless a specially devised sampling rod is at hand. In order to get an average of the bin it is necessary to draw portions from it at all depths and at both ends. The best form of apparatus which the writer has seen for doing this, consists of a long iron rod such as is shown in Fig. 38.

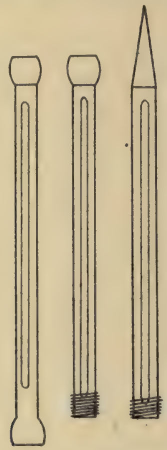

Fig. 38 Jointed Sampling Rod.

It is made of 1 inch wrought iron piping and in sections of about four feet each, to allow of its being readily carried about from one mill to another. The couplings are long and are turned down so as to taper at either end. In the end of the rod is fastened a steel point and slots about ½ inch in width and fourteen inches in length are cut in each section as shown in the illustration. One side of each slot is made to project slightly beyond the side of the pipe and sharpened, as shown in the section *A-B*. In using the rod, as many sections are used as may be necessary to reach to the bottom of the bin. These are joined, the whole is thrust into the bin until it reaches the bottom, the rod is filled by turning it a few times, then withdrawn, turned upside down and the cement shaken out of it into a bag by rapping it against the side of the stock house.

A rod made with the slot running its entire length and terminating in a *T*, with two pieces of short pipe screwed into it to form a handle, is sometimes used to sample bins. The main trouble with this rod is that such a long slot weakens the sampler, and unless made of very heavy pipe it soon twists out of shape. Grain samplers may also be used to sample bins, but are seldom made long enough to reach the bottom of the bins.

A vacuum sampling apparatus invented by Bertram Blount, the English cement expert, is described in The Chemical Engineer, January, 1905, p. 161, which consists first of a small iron pipe some ⅜-inch in bore, with one end closed and drawn to a point. The other end is open, and to it can be attached a length of rubber tubing. The pointed end of the pipe has a number of small holes pierced in it, and to take a sample this tube is thrust into the heap of cement. It may be pushed in at any angle from vertical downwards. The india-rubber tube above referred to is connected to a drum provided with an opening covered with a screw cap, the whole being made air-tight. The apparatus is completed by means of an exhausting pump which may either be worked by hand or by a small motor. It is also connected to the drum by a length of rubber tubing. Each length of rubber tubing is provided with a screw slip, which can be made to nip the tubing so tightly that no air can get past.

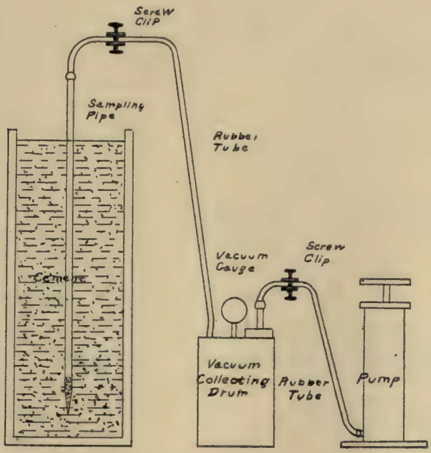

Fig. 39, Blount's Vacuum Sampler.

In sampling the iron pipe is plunged nearly to the bottom of the cement. The amount of cement which is forced through the small holes in the lower end of the pipe during this process is so small that it may be neglected. The clip on the rubber tube joining the sampling pipe with the drum is then screwed up. A man then worked the pump, and exhausts the drum until a vacuum equal to some 18 or 20 inches of mercury has been produced, when the clip on the tube between the drum and the pump is screwed up. The drum has fitted to it a gauge, so that the amount of vacuum in it may be readily seen. The clip on the tube between the sampling pipe and the reservoir drum is then unscrewed, with the result that a certain amount of cement will be drawn through the small holes in the sampling pipe, up through the latter, and then conveyed thence through the rubber tube to the reservoir. The whole process takes but a minute or two, and the amount drawn into the reservoir varies with the vacuum produced. Several samples may be taken if desirable, and the whole operation requires but half an hour.

DETERMINATION OF SILICA, FERRIC OXIDE AND ALUMINA, LIME AND MAGNESIA.

Method Proposed by the Committee on Uniformity in the Analysis of Materials of the Portland Cement Industry of the New York Section of the Society of Chemical Industry.[1]

Solution.

One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for 15 minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 cc. of strong HCl added and digested

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[1] This committee consisted of Messrs. Clifford Richardson, Spencer B. Newberry and H. A. Schaffer. Their various reports were published in *Journal of the Society of Chemical Industry*, XXI, **12**, 830 and 1216; *Journal American Chemical Society*, XXV. **1180** and XXVI 995; and *Cement and Engineering News* XVI, 37.

with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.[1] The solution is then evaporated to dryness, as far as this may be possible on the bath.

Silica.

The residue without further heating is treated at first with 5 to 10 cc. of strong HCl which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for 10 minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for 15 minutes and checked by a further blasting for 10 minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cc. of HFl and four drops of H_2SO_4 and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.[1]

Al_2O_3 and Fe_2O_3,

The filtrate, about 250 cc., from the second evaporation for SiO_2, is made alkaline with NH_4OH after adding HCl, if need be, to insure a total of 10 to 15 cc. strong acid, and boiled to expel excess of NH_3, or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the beaker in which the precipitation

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[1] If anything remains undecomposed it should be separated, fused with a little Na_2CO_3 dissolved and added to the original solution. Of course a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

[1] For ordinary control work in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never.

was made. The aluminum and iron are then reprecipitated by NH_4OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted 5 minutes, with care to prevent reduction, cooled and weighed as $Al_2O_3 + Fe_2O_3$.[2]

CaO.

To the combined filtrate from the $Al_2O_3 + Fe_2O_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 cc. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC_2O_4 assumes a well-defined granular form. It is then allowed to stand for 20 minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl, and the solution made up to 100 cc. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of Al_2O_3 separates this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered, and washed.[3] weighed as oxide by ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.[4]

MgO.

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam-bath to about 150 cc., 10 cc. of saturated solution of $Na(NH_4)HPO_4$ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium ortho-phosphate

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[2] This precipitate contains TiO_2, P_2O_5, Mn_3O_4.

[3] The volume of wash water should not be too large; vide Hillebrand.

[4] The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to about 100 cc., 1 cc. of a saturated solution of $Na(NH_4)HPO_4$ added, and ammonia drop by drop, with constant stirring until the precipitate is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about 2 hours when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $Mg_2P_2O_7$.

Method Proposed by the Committee on the Uniform Analysis of Cement and Cement Materials of the Lehigh Valley Section of the American Chemical Society.[1]

Weigh out .5 gram into a wide platinum dish of about 50 cc. capacity; add a very little water and break up lumps with a glass rod; add 5 cc. hydrochloric acid (1-1) and evaporate to dryness at a moderate heat, continuing to heat the mass—not above 200° C.—until all odor of acid is gone. Do not hurry this baking or skimp the time. The whole success of the analysis depends on thoroughness at this point. Cool; add 20 cc. hydrochloric acid (1-1); cover and boil gently for ten minutes; add 30 cc. water, raise to boiling, and filter off the silica; wash with hot water four or five times; put in crucible, ignite (using blast for 10 minutes), and weigh as SiO_2.

Iron and Alumina.

Make filtrate alkaline with ammonia, taking care to add only slight excess; add a few drops of bromine water and boil till odor of ammonia is faint. Filter off the hydroxides of iron and aluminum, washing once on the filter. Dissolve the precipitate with hot dilute nitric acid, reprecipitate with ammonia; boil five minutes; filter and wash the iron and alumina with hot water once; place in crucible, ignite carefully, using blast for 5 minutes, and weigh combined iron and aluminum oxides.

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[1] This committee was appointed at a meeting of the Lehigh Valley Section of the American Chemical Society, held November 18, 1903, and consisted of Messrs. Wm. B. Newberry Richard K. Meade and Ernest B. McCready. Their report was published in *Cement and Engineering News*, August, 1904, and embodies the methods most acceptable to the chemists actively employed in the cement industry as ascertained by correspondence with these chemists themselves.

Lime.

Make the filtrate from the hydroxides alkaline with ammonia; boil; add 20 cc. boiling saturated solution ammonium oxalate; continue boiling for five minutes; let settle and filter. Wash the calcium oxalate thoroughly with hot water using not more than 125 cc., and transfer it to the beaker in which it was precipitated, spreading the paper against the side and washing down the precipitate first with hot water and then with dilute sulphuric acid (1-4); remove paper; add 50 cc. water, 10 cc. conc. sulphuric acid, heat to incipient boiling and titrate with permanganate[1], calculating the CaO.

Magnesia.

If the filtrate from the calcium oxalate exceeds 250 cc., acidify, evaporate to that volume; cool, and when cold add 15 cc. strong ammonia and with stirring 15 cc. stock solution of sodium hydrophosphate. Allow to stand in the cold six hours or preferably over night; filter; wash the magnesium phosphate with dilute ammonia (1-4 + 100 gms. ammonium nitrate per litre) put in crucible, ignite at low heat and weigh the magnesium pyrophosphate.

NOTES.

Of the above schemes, the first is undoubtedly the more accurate of the two. It does not seem practicable, however, to use it in the everyday routine work of the mill laboratory. It also requires a rather high degree of manipulative skill to carry out the additional steps in its performance. When very accurate determinations are required, it will undoubtedly give better results than the second scheme, provided the analysis is skilfully executed. On the other hand, under the conditions usually met with in the laboratories of cement manufacturers and large users, where rapidity, coupled with a moderate degree of accuracy is required, and where one man is required to run a number of analyses per day, the second scheme will unquestionably give more satisfaction, if properly carried out.

A good well-made Portland cement is practically entirely soluble in hydrochloric acid. Fusion, therefore, with sodium or potas-

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[1] See "Volumetric Determination of Lime," page 185.

sium carbonate is rarely necessary. It is also objectionable, for when calcium and magnesium are precipitated, as oxalate and phosphate respectively, from solutions containing much sodium or potassium salts, the precipitates are almost sure to be contaminated with alkaline salts. Even much washing fails to remove the impurity from the precipitate. When, therefore, the sample of cement has been fused directly with from 3 to 5 grams of sodium carbonate, there is sure to be this danger that the lime and magnesia precipitates will carry down some sodium salts, from which subsequent washing will fail to free them. In accurate work this error can be eliminated by reprecipitation. If instead of fusing the sample directly with five to ten times its weight of sodium carbonate, the impure silica, separated by treatment with hydrochloric acid, is fused with an equal bulk of sodium carbonate, the quantity of sodium salts introduced into the solution will be reduced to one-fourth, usually between 1.0 and 1.5 gram of sodium chloride.

Should the cement prove to leave a considerable residue of silicious matter on dissolving in acid, the best plan will be to weigh out a new sample and pursue the following method suggested by Dr. Porter W. Shimer, Easton, Pa.:

Weigh ½ gram of the finely ground dried cement into a platinum crucible and mix intimately, by stirring with a glass rod, with 0.5 gram of pure dry sodium carbonate. Brush off the rod into the crucible with a camel's hair brush. Cover the crucible and place over a low flame. Gradually raise the flame until the crucible is red hot and continue the heating for five minutes longer; then place over a blast lamp and heat five minutes more. While still hot, plunge the bottom of the crucible half the way up into cold water. This will loosen the mass. Drop the mass into a casserole or dish and cover the latter with a watch glass. Pour into the crucible a portion of a mixture of 30 cc. of hot water and 10 cc. of dilute hydrochloric acid. Heat on a hot plate, and then pour into the dish or casserole. Clean out the crucible with a rubber-tipped rod, using the rest of the acid and water. The quantity of sodium salts introduced into the solution from 0.5 gram of carbonate is so small that possible contamination of the lime and magnesia precipitates is done away with. On heat.

ing cement and sodium carbonate together in this proportion no fusion takes place, only a sintering.

Some operators[1] make the amount of residue left on solution with acid a test of the thoroughness with which the cement has been made. Peckham uses a 10 per cent. solution of hydrochloric acid and 5 grams of cement just as received, making the solution slowly and with care. Blount dissolves the cement in strong hydrochloric acid, evaporates the solution to dryness, but not intentionally baking the evaporated material, redissolving in hydrochloric acid, filters, washes, dissolves the precipitated silica with sodium carbonate solution and collects, ignites and weighs the final insoluble residue.

If this test is to be made use of to check the burning and proper grinding and mixing of the raw materials the process of Blount is more nearly correct, since it is not effected so much by the conditions under which solution is effected. The quantity of silica which will be left on treating cement with acid will depend not only upon the chemical composition of the cement, but also upon the fineness to which the sample is ground, strength of acid, etc. Coarsely ground material giving much more residue than finely ground. Cement passing a 50-mesh sieve, but retained by a 100, will give much more silica than that passing a 100-mesh, but retained on a 200-mesh, yet neither has binding properties in the ordinary sense of the word, so that the contention made that the silica which does not dissolve even though it may come from good properly burned material, still comes from inert particles, and is therefore not in a form of active combination, is not logical because by grinding these inert particles a little finer we can considerably reduce the silica left without increasing any their hydraulic value. Many silicates are also soluble in acid, which have no hydraulic properties, such as slags, so that all the silica which goes into solution is not necessarily combined in such a way as to form hydraulic compounds.

The test as applied by Blount does not seem of much practical value, either. Of course, when the residue of uncombined silica is large, it shows something is wrong with the cement, but this

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[1] **Peckham** : *J. S. Chem. Ind.* XXI, 831 and *J. Amer. Chem. Soc.* XXVI, 1636 and Blount *J. Am. Chem. Soc.* XXVI, 995.

fact is usually revealed much more satisfactorily by the tests for soundness which property is dependent on the proper combination of the silica with the lime. A marl containing a per cent. or so of silica in the form of quartz grains would probably give a cement containing from ½ to 1 per cent. of insoluble or uncombined silica, yet if this quartz had been taken into consideration in proportioning the raw materials, this cement might easily be better than one which gives no free or uncombined silica, because the latter might be unsound. Also, as we have said before, all the silica, which is reported as combined is not necessarily so combined as to form Portland cement.

At the mill itself, there is little knowledge to be gained by the test as used by either Peckham or Blount, as the soundness test, coupled with the usual determinations, will tell us whether the fault is due to faulty manufacture or improper proportioning of the raw materials.

Alex. Cameron,[1] in 1894, pointed out the fact that no matter how many evaporations were made in determining silica, accurate results could not be obtained unless a filtration intervened between each one. This paper seems to have escaped the notice of most chemists and was only brought to their knowledge by Dr. W. F. Hillebrand,[2] in 1901, in a paper read at a meeting of The American Chemical Society, in Philadelphia, in December of that year, in which he gave the results of his own experiments along that line. It was in accordance with his suggestion that the committee of the New York Section of the Society of Chemical Industry advised the double evaporation with intervening filtration, which they inserted in their scheme. There is no question but that Dr. Hillebrand is right and that this procedure is necessary in very accurate work. In the analysis of Portland cement, a residue of silica, amounting to from two to four milligrams, can usually be obtained by evaporation of the filtrate from the first silica precipitate to dryness, still the extra step is tedious, and adds considerably to the time necessary for making an analysis. It is also true, however, that there is considerable iron and alumina carried down with the silica, and that these two errors

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[1] *Jour. Amer. Chem. Soc.* XXIV, 362.
Chem. News, LXIX, 171.

will balance each other to a great extent, so that the amount of silica reported is seldom more than one or two-tenths of a per cent. low. Below are some figures upon this.

Cement No.	A Per cent. Silica after one evaporation and dehydration at 200° C.[1]	B Impurities in this precipitate.	C Additional Silica recovered by a second evaporation.	D Silica in the iron and alumina precipitate.	E Total Silica, columns (A + C + D) — B[2].	Error in column A.
1	19.95	0.35	0.38	0.09	20.07	—0.12
2	20.18	0.31	0.42	0.12	20.41	—0.23
3	20.46	0.37	0.36	0.08	20.53	—0.07
4	21.12	0.38	0.24	0.05	20.03	+ 0.09
5	21.63	0.34	0.32	0.14	21.75	—0.12
6	22.45	0.41	0.34	0.01	22.49	—0.04

Silica is hard to wash and retains alkalies tenaciously. It is well for the inexperienced operator, until he finds out how much washing is required, to test with silver nitrate, and continue the operation until the washings cease to react for chlorides.

Silica may be ignited wet, but care must be taken not to dry the precipitate too quickly over the flame, else the steam in escaping will carry with it fine particles of silica. The best plan is not to place the crucible at first directly over the burner, but instead to one side of a low flame. The silica must be ignited over a blast lamp in order to drive off the last traces of water, which it holds most tenaciously. Ignition over a Bunsen burner, even for some hours, is insufficient for complete dehydration. The blast lamp will also help to burn off the last trace of the carbon of the filter paper.

The purity of the silica can easily be tested, and indeed in

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[1] This represents the silica which would be found by the method of the committee of the Lehigh Valley Section of the American Chemical Society.

[2] This represents the silica actually present in the sample.

accurate work, it should always be done. After burning off the carbon, igniting over a blast and accurately weighing, moisten the silica with dilute sulphuric acid and then half fill the crucible with C. P. hydrofluoric acid. Incline the crucible on a tripod over a burner turned low, in such a way that the flame plays under the upper part of the crucible. This causes a rapid evaporation of the solution. When no more fumes come from the crucible move the burner back until it plays upon the bottom of the crucible and raise the flame until the crucible is cherry-red. Cool and weigh. The loss represents silica, SiO_2, and the residue in the crucible is usually alumina. Its weight may be added to that of the iron and alumina found by precipitation with ammonia, or the residue may be dissolved in concentrated hydrochloric acid and added to the filtrate from the silica, before the addition of ammonia.

If silica is to be purified, however, it is also necessary, not only to make the double evaporation with intervening filtration, but also to determine the silica in the iron and alumina and add it to the weight of the purified silica. Unless this is done the silica will be too low and the iron and alumina too high.

Alumina, Al_2O_3, is soluble to some extent in a large excess of ammonia. If, however, the excess is expelled by boiling, the alumina is again precipitated. The presence of ammonium chloride in the solution greatly aids in the separation of alumina by ammonia. The precipitate of iron and alumina must be filtered off promptly since the alkaline liquid will absorb carbon dioxide from the air, forming calcium carbonate which would be filtered off with the iron and alumina. For the same reason, when for any cause the filtrate from the iron and alumina has to stand some days, it should be acidified with hydrochloric acid before setting aside. This is necessary when the calcium is to be determined volumetrically, and it saves trouble elsewhere, since the deposit of calcium carbonate forms as a crust on the sides and bottom of the beaker, and is very difficult to remove, without solution and reprecipitation.

To avoid time lost in boiling off a large excess of ammonia, only a very slight excess of this reagent should be added. The bottle shown in Fig. 40 will be found very useful in ammonia precipitations, as the addition can be made drop by drop, if desired, and the quantity added regulated so as to give the liquid only a faint odor of ammonia.

Magnesium hydroxide, $Mg(OH)_2$, is not completely soluble in ammonia. The precipitate is, however, readily soluble in ammonia solutions, containing sufficient ammonium chloride. The precipitation of the magnesia along with the iron and alumina is insured against by the formation of ammonium chloride, which takes place before the iron and alumina are precipitated, on adding ammonia to the hydrochloric acid solution. If preferable, the operator can be on the safe side by adding half a gram of the salt itself (ammonium chloride) to the filtrate from the silica before precipitating the iron and alumina. The presence of ammonium chloride is also necessary for the complete precipitation of the alumina.

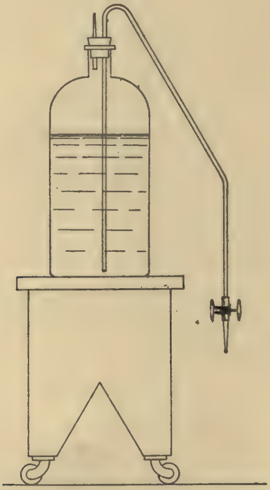

Fig. 40, Apparatus for Ammonia Precipitation.

The precipitate of iron and alumina always contains more or less lime and magnesia, from which long washing fails to free it. Solution and reprecipitation are, therefore, necessary to get around the difficulty. The precipitate is very apt to contain traces of silica also. Some of this comes from the action of the ammonia on the reagent bottle in which it is kept, some from the action of the alkaline liquid on the beaker in which the precipitation was made, and some which failed to be separated by evaporation in the proper place is also carried down here. Since the impurity usually present in the silica is alumina and that in the alumina is silica, the two sources of error tend to balance each other. If desired the weighed precipitate of ferric oxide and alumina can be dissolved by fusion with potassium bisulphate for some hours, the fused mass dissolved in water, a few drops of sulphuric acid added and the solution evaporated until fumes come off in quantity. The residue is then collected after cooling and diluting the solution,[1] and weighed as $SiO._2$

Ammonia water takes up silica rapidly from the glass container, hence when accurate work is desired and purification of silica and alumina are to be undertaken, it is necessary to redistill the ammonia over lime. This should be done every week or two at least. Even for technical work it is not a bad plan, as there is no telling how long the ammonia has stood on some dealer's shelves. The still may be kept set up in a corner of the hood and the operation conducted by the laboratory boy. By using redistilled ammonia it is possible to do away with the second precipitation of the iron and alumina, which is made necessary by the presence of ammonium carbonate in the ammonia water, as this carbonate precipitates some calcium carbonate along with the alumina.

The precipitate of iron and alumina is troublesome to wash, and unless it is freed from chlorides, some loss of iron, by volatilization as ferric chloride, will result when the precipitate is ignited. In order to avoid this tedious washing, the writer has always followed the plan of dissolving the first precipitate in nitric acid, thus avoiding the presence of chlorides in the second precipitate and doing way with the tedious washing. When this is done only enough washing is necessary to collect the precipitate in the point of the filter. This plan is suggested in the method of the Lehigh Valley Committee.

Calcium oxalate may be washed with hot water. Some chemists prefer to add a little ammonia to the wash water, but to the

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[1] Hildebrand, *Jour. Amer. Chem. Soc.*, XXIV., 369.

author this seems unnecessary. The precipitate should always be formed in a boiling ammoniacal solution, with stirring, and allowed to settle before filtering. Some chemists heat the ammonium oxalate solution also to boiling before adding to the boiling solution containing the calcium. Sufficient ammonium oxalate should always be added to convert all the magnesium present as well as the calcium to oxalate, else the precipitation of the calcium will be incomplete. Nothing is gained by allowing the lime more than 15 or 20 minutes to settle.

Magnesium oxalate is not very soluble and if magnesia is present in large amount will be precipitated with the lime. On the other hand, calcium oxalate is slightly soluble in hot water. As cement contains such a small percentage of magnesia the quantity carried down with the lime is usually less than 0.1 per cent., and as the quantity of calcium oxalate which goes into solution is precipitated with the magnesia, the two errors tend to balance each other. The factors entering into a clean separation of lime and magnesia are that there must be an excess of ammonium oxalate and that the solution should measure at least 300 cc.

Directions for making the solution for determining lime volumetrically and for carrying out the process will be found on page 185. The volumetric determination is very accurate and under ordinary technical conditions, when many analyses are made every day, will prove as trustworthy as the gravimetric. When an occasional determination only is made the latter will prove more useful.

Calcium oxalate on ignition over a burner to very faint redness changes to calcium carbonate. If the heating is increased and the blast is used calcium oxide is formed. Instead of weighing as the oxide some chemists prefer to weigh as a sulphate. To do this,[1] dry the precipitate perfectly, detach it as far as possible from the filter to a piece of black glazed paper. Burn the filter-paper in a weighed platinum crucible, and when all carbonaceous matter is burned, brush the precipitate into the crucible from the glazed paper. Drop concentrated sulphuric acid on the precipitate till it is well moistened, avoiding an excess, and heat

[1] Lord, "Notes on Metallurgical Analysis," p. 11.

the crucible under a hood cautiously, from a burner held in the hand, until the swelling of the mass subsides and the excess of sulphuric acid has been driven off, as shown by the disappearance of the white fumes coming from the crucible. Then heat for five minutes to a cherry red heat, but do not use the blast. Cool and weigh as calcium sulphate, which multiplied by 0.41185 gives the equivalent of lime, CaO.

Mr. W. H. Hess uses the following method[1] for converting the calcium oxalate to calcium sulphate. After burning off all the carbon of the filter-paper, the crucible is allowed to cool partly, when a portion of chemically pure dry ammonium nitrate, approximately equal in bulk to the lime in the crucible, and about twice as much chemically pure fused ammonium sulphate are added. A tight-fitting cover is now placed on the platinum crucible and then gentle heat is applied. Mr. Hess found it very convenient to incline the crucible at an angle of 30°, allowing the tip of the crucible cover to project outward, and then apply the flame to the tip of the cover, gradually bringing the flame under the crucible as the reaction grows less and less violent. The reaction is complete when fumes of ammonia salts are no longer driven off. Intense ignition is unnecessary and is to be avoided. The crucible should be weighed with its cover.

The evaporation of the filtrate from the lime may be rapidly carried out, in a large porcelain dish, in the following manner: Place a piece of wire gauze on a tripod and in the centre of this, lay a disk of asbestos paper, the size of a silver dollar. Now set the dish on the gauze and place a Bunsen burner, with its flame turned low, so that the latter comes under the asbestos. The solution will then evaporate rapidly, and yet without ebullition, or loss by spurting.

Magnesium pyrophosphate is quite soluble in hot water, less so in cold water, and practically insoluble in water rendered strongly ammoniacal. It should be washed, therefore, with a mixture of water and ammonia. Some chemists use no ammonium nitrate in their washing fluid, and mix in proportions varying from ten to three parts water for one part of ammonia. It is a difficult precipitate to ignite perfectly white, but the blast

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[1] *Jour. Amer. Chem. Soc.*, **22**, 477.

lamp should never be used in the attempt to make it so, as destruction of the platinum crucible might follow. The precipitate may be ignited wet if a low flame is used at first.

A Gooch crucible may be used in place of a filter paper, although it is much less convenient. It consists of a flat-bottomed, perforated crucible provided with a cap (Fig. 41). The perforated crucible is placed in one end of a piece of soft rubber tubing of large bore, the other end of which is stretched over a small funnel passing into a flask through a rubber stopper (Fig. 42). The flask is connected with the filter pump. To prepare the filter, pour a little prepared asbestos (purified by washing with hot concentrated hydrochloric acid) suspended in water into the crucible and attach the suction to the flask. The asbestos at once forms a thick felt over the bottom of the crucible, which by using the suction may be readily washed with water. After washing, suck dry as possible with the pump, remove from the funnel, detach any pieces of asbestos that may be on the outside of the bottom of the crucible, cap, ignite, and weigh. Remove the cap, attach to the funnel as before, apply the suction and pour the liquid to be filtered through the crucible, wash, cap, dry, if necessary, ignite and weigh as before. The crucible and cap may be purchased from dealers in platinum or chemical ware.

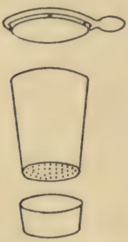

Fig. 41, Gooch Crucible.

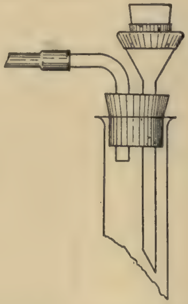

Fig. 42, Gooch Crucible in Use.

The use of platinum dishes is recommended for the solution and evaporation of the sample because platinum is a much better conductor of heat than porcelain and glass, and consequently evaporations can be carried out much more rapidly in them than in anything else. There is also no danger of contaminating the analysis with silica from the dish.

Crucibles in which silica has been ignited may be most conveniently cleaned by boiling in them a little hydrofluoric acid. Crucibles used to ignite iron and alumina are best cleansed by boiling in them dilute (1-1) hydrochloric acid, while those used for barium sulphate can be cleaned by strong sulphuric acid and warming. Magnesium pyrophosphate may be readily removed from platinum or porcelain crucibles by placing the latter in a beaker of ten per cent. hydrochloric acid and boiling. The dilute acid in this case will do the work when strong acid will fail. No appreciable loss in weight of the crucible will be occasioned by any of the above treatments.

VOLUMETRIC DETERMINATION OF LIME.

Preparation of the Standard Permanganate.

Dissolve the quantity of pure crystallized potassium permanganate shown in the table below, in the desired amount of water, using a balance accurate to at least 0.5 per cent. of the weight of permanganate to be taken, and measuring the water with a graduated flask. In this way, a solution can be made of sufficiently near the correct strength for the use of the table in the appendix.

Table XX.—for Preparing Standard Permanganate of Approximately the Strength 1 cc. = 0.005 Gram CaO.

5.64	grams	$KMnO_4$	to	1	liter	of	water
11.28	“	“	“	2	“	“	“
16.92	“	“	“	3	“	“	“
22.56	“	“	“	4	“	“	“
28.20	“	“	“	5	“	“	“
33.84	“	“	“	6	“	“	“
39.48	“	“	“	7	“	“	“
45.12	“	“	“	8	“	“	“
50.76	“	“	“	9	“	“	“
56.40	“	“	“	10	“	“	“

Use a balance accurate to at least 0.5 per cent. of the weight of $KMnO_4$ to be taken and measure the water with a graduated flask.

The simplest way to make the solution, is to weigh out the permanganate and place in the bottle with the water, some week or ten days before the solution is to be standardized. The contents of the bottle, which is kept in a dark place, is shaken every now and then for the first two or three days. When the solution is needed, it is siphoned off into another bottle, leaving about an inch of solution in the old bottle. A glass siphon is used and its end should not extend nearer than an inch from the bottom of the bottle. The solution in the new bottle is now shaken and standardized. The writer in his laboratory used eight liter (2 gallon bottles) and this quantity of permanganate will last him from two to three weeks. The solution should be standardized every week. It will be found more convenient to make the solution as above and standardize every week, than to attempt to make a solution which will not change, by boiling and filtering as directed by Morse.[1]

The permanganate solution should be kept in a dark place. Fig. 43 shows the arrangement for storing and using the permanganate adopted by the writer.[2]

Standardizing the Permanganate.

To standardize the permanganate, weigh into a 400 cc. beaker 0.5 gram of powdered calcite; add 100 cc. of water and 10 cc. of hydrochloric acid, cover with a watch glass and boil until all carbon dioxide is expelled. When completely dissolved, dilute to the usual volume in which the lime precipitation is made in an analysis, and make alkaline with ammonia. Add 20 cc. of a boiling saturated solution of ammonium oxalate, continue boiling and stirring for a few minutes, let settle, filter and wash thoroughly with hot water using not more than 125 cc. of the liquid. Transfer the filter and precipitate to the beaker in which the precipitation was made, spreading the paper against the side and washing down the precipitate first with hot water and then with dilute sulphuric acid (1-4). Remove the paper, add 50 cc. of water and 10 cc. concentrated sulphuric acid, heat to incipient boiling and titrate with permanganate. The factor for lime, CaO, is found by dividing 0.56 by the number of cubic centimeters of permanganate taken and for calcium carbonate, $CaCO_3$, by dividing 100 by the number.

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[1] *Amer. Chem. Jour.*, XVIII., 401.

[2] *Chemical Engineer*, I., 288.

The above method is that recommended by the Committee of the Lehigh Valley Section of the American Chemical Society on the Uniform Analysis of Cement and Cement Materials. Some operators prefer to use ferrous ammonium sulphate for standardizing. The usual method of using this is as follows:

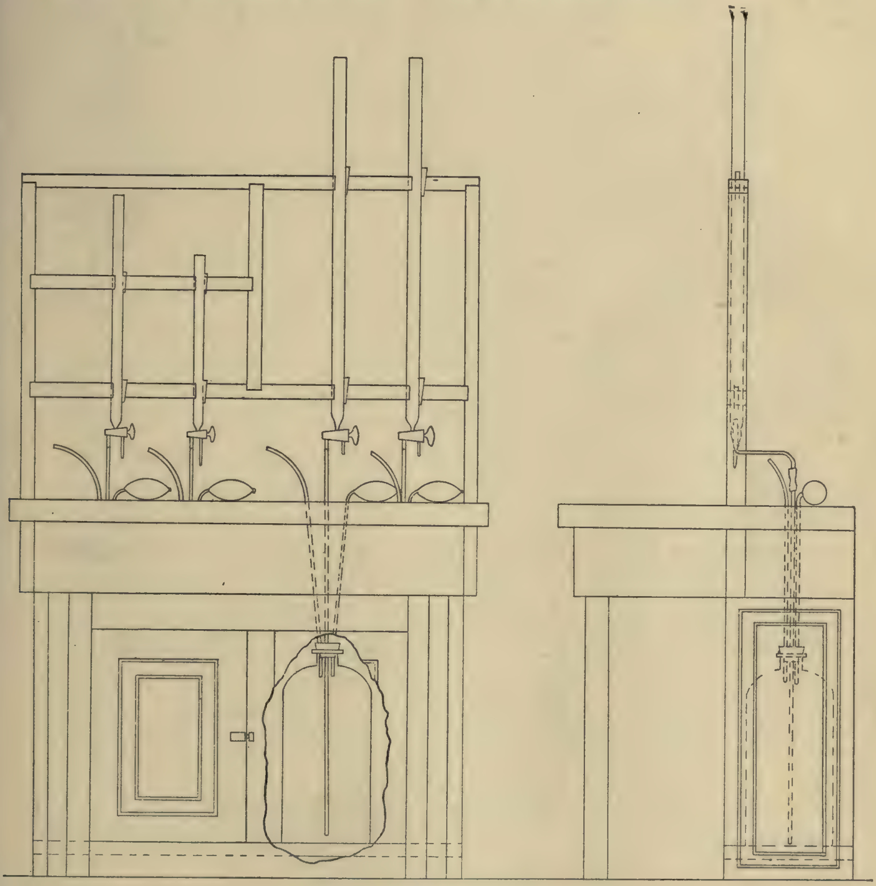

Fig. 43, Table for Titrations.

Weigh into each of two beakers 1.4 grams of pure crystallized ferrous ammonium sulphate, add cold water, allow the salt to completely dissolve without stirring and then add 10 cc. of dilute sulphuric acid. Stir and run in the permanganate from a burette until the color of the solution in the beaker just changes to pink. The weight of the double salt used divided by 14, and then by the number of cubic centimeters of permanganate required, will give the lime, CaO, value per cubic centimeter, for the permanganate. The duplicate titrations should check closely; if not, another pair should be run. For other methods of standardizing the permanganate solution see "Determination of Ferric Oxide."

Calcite in the form of Iceland Spar can be obtained of great purity, and may be generally taken as 100 per cent. $CaCO_3$. In purchasing a new lot it should be specified that the purest grade is wanted "for standardizing." On receipt it should be powdered to pass a 100-mesh sieve and kept in a glass-stoppered bottle. From this a small portion should be taken and placed in an ounce wide mouth bottle, provided with either a glass or rubber stopper. This small sample should be dried at from 100-110° C., and on removal from the drying oven kept tightly stoppered. The calcite should then be checked by a careful analysis for silica, iron oxide and alumina and the lime determined gravimetrically as on page 172. A blank should be run at the same time; that is, a dish is selected and acid added to it just as if it contained a sample, etc. The small residues found after each step should be deducted from those found on analysis of the calcite. The sample used in the writer's laboratory gave less than 0.1 per cent. impurities when treated in this manner and 56.02 per cent. lime, so for practical purposes it has been considered as 100 per cent. pure. The small sample of calcite should be dried after the bottle has been opened for five or six determinations, as it will take up some moisture from the air.

The Determination.

Directions for determining the lime volumetrically are given on page 174.

Notes.

The method depends upon the reaction between oxalic acid and potassium permanganate.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

The reaction between iron and permanganate is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Hence 5 molecules $H_2C_2O_4 = 2$ mols. $KMnO_4 = 10$ mols. $FeSO_4$ or 5 mols. $H_2C_2O_2$ (= 5 mols. CaO) = 10 mols. $FeSO_4$ (= 10 atoms Fe).

Then 5 mols. CaO = 10 atoms Fe, and 5(40 + 16) CaO = 10 × 56 Fe, or 280 CaO = 560 Fe.

Hence, CaO : Fe :: 280 : 560, from which $CaO = \frac{280}{560}$ Fe or $\frac{1}{2}$Fe.

So the iron value of any permanganate solution divided by 2 will give its lime value.

The titration with permanganate must be made with a hot solution between 60° and 70° C. In the scheme given, the solution is heated by the action with the strong sulphuric acid, added just before titration.

RAPID DETERMINATION OF LIME WITHOUT SEPARATION OF SILICA, ETC.[1]

Weigh 0.5 gram of cement into a dry 500 cc. beaker and add, with constant stirring, 20 cc. of cold water. Break up the lumps and when all the sample is in suspension, except the heavier particles, add 20 cc. of dilute (1-1) hydrochloric acid and heat until solution is complete. This usually takes 5 or 6 minutes. Heat to boiling and add dilute ammonia (0.96 sp. gr.) carefully to the solution of the sample until a slight permanent precipitate forms. Heat to boiling and add 10 cc. of a 10 per cent. solution of oxalic acid. Stir until the oxides of iron and aluminum are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 cc. of boiling water and sufficient (20 cc.) saturated solution of ammonium oxalate to precipitate the lime. Boil and stir for a few moments, remove from the heat, allow the precipitate to settle and filter on an 11 cm. filter. Wash the precipitate and paper ten times with hot water using not more than 10 or 15 cc. of water each time. Remove the filter from the funnel, open and lay against the sides of the beaker in which the precipitation was made, wash from the paper into the beaker with hot water, add dilute sulphuric acid, fold the paper over and allow to remain against the walls of the beaker. Heat to 80° C. and titrate wtih standard permanganate until a pink color is obtained, now drop in the filter paper, stir until the color is discharged and finish the titration carefully drop by drop.

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[1] *Chemical Engineer*, I, 21.

Notes.

The above method for the determination of lime is dependent on the fact that lime can be completely precipitated as oxalate in solutions containing free oxalic acid, while iron, alumina and magnesia are not. The method as outlined above was worked out by the writer some years ago and has been in constant use in the laboratories of several large cement companies since that time, giving entire satisfaction.

The oxalic acid method is much more accurate than the one sometimes used of precipitating the iron and alumina by ammonia and then without filtration throwing down the lime as oxalate in the same solution, since in the latter method some of the lime is thrown down as carbonate and hence not found by the permanganate. It is just as rapid as the above because the only extra step is the addition of 10 cc. of oxalic acid solution which is more than made up for by the more rapid filtration due partly to the fine granular precipitate of calcium oxalate obtained and also to this not being contaminated by the flocculent alumina precipitate.

The oxalic acid method is just as accurate as the longer one of separating the silica, iron, and alumina from the solution, before precipitating the lime. Indeed unless the iron and alumina are separated by double precipitation it is the more accurate of the two.

A determination can be made by the above method in from 25 to 30 minutes, of which 10 or 15 are required for the lime to settle. The ammonia must not be added in very large excess and to guard against this the addition can best be made from the bottle shown in Fig. 40, on page 180.

DETERMINATION OF FERRIC OXIDE.

By Titration with Potassium Permanganate. (Marguerite's Method.)

Standard Potassium Permanganate.

Dissolve 1.975 grams of pure crystallized potassium permanganate in 100 cc. of water, boil and allow to stand all night. In the morning filter through asbestos into a bottle and dilute to 1 liter. To test, or standardize, the solution, weigh into each of two beakers 0.4900 gram of pure ferrous ammonium sulphate, equivalent to 0.1 gram of ferric oxide, Fe_2O_3. Dissolve in 50 cc. of water, without heating, add 10 cc. of dilute sulphuric acid and run in the permanganate from a burette until the color of the solution in the beaker just begins to turn pinkish. Take the reading of the burette and then add another drop, which should cause the solution to become decidedly pinkish. Divide the weight of ferric oxide (0.1 gram) equivalent to the weight of ferrous ammonium sulphate taken for the titration (0.49 gram) by the number of cubic centimeters of permanganate required; the result will give the ferric oxide equivalent to 1 cc. of the permanganate.

To use iron wire in standardizing, clean two pieces of fine iron wire, weighing 0.1 gram each, by rubbing first between emery paper and then with a cloth. Coil around a lead pencil and weigh each coil. Put 30 cc. of dilute sulphuric acid in a strong gas bottle provided with a perforated stopper through which passes a perfect fitting glass tube with a hole blown in its side (Fig. 44). Heat the acid to boiling and drop in a coil of wire. When the solution of the latter is complete, remove the bottle from the source of heat and, after closing the opening by pushing the perforated glass tube down until its opening is closed by the stopper, allow the gas bottle to cool. When cold titrate the solution with the permanganate solution as above. Multiply the weight of the iron wire by 0.003 and deduct the result from the original weight for impurities. Multiply the corrected weight by 1.4286, or divide by 0.7, and divide by the number of cubic centimeters of permanganate required. The result will be the ferric oxide equivalent of 1 cc. of the standard potassium permanganate. Repeat the test with the other weighed coil of iron wire. The values for each cubic centimeter of permanganate by the two titrations should agree closely. Yet another way is to dissolve the iron wire in 15 cc. of dilute sulphuric acid in a beaker, cool,

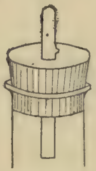

Fig. 44, Stopper and Valve for Iron Reductions.

dilute, pass through the reductor, described on page 191, and titrate with the permanganate, calculating the results as above.

The Determination.

The Committee on Uniformity in Analysis of Materials for the Portland Cement Industry, of the New York Section of the Society of Chemical Industry, recommend that the determination of ferric iron be conducted on the ignited precipitate of ferric oxide and alumina, after weighing, in the following manner:

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of $KHSO_4$, or, better, $NaHSO_4$, the melt taken up with so much dilute H_2SO_4 that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water the small amount of silica is filtered out, weighed, and corrected by HFl and H_2SO_4[1]. The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards whilst passing CO_2 through the flask, and titrated with permanganate.[2] The strength of the permanganate solution should not be greater than .0040 gr. Fe_2O_3 per cc.

The Committee appointed by the Lehigh Valley Section of the American Chemical Society direct also that the determination shall be carried out on the precipitate of oxide of iron and alumina. Their method differs from the above chiefly in the manner of reduction, and is as follows:

Add four grams acid potassium sulphate to the crucible containing the ignited oxides of iron and alumina, and fuse at a very low heat until oxides are wholly dissolved—twenty minutes at least; cool; place crucible and cover in small beaker with 50 cc. water; add 15 cc. dilute sulphuric acid (1-4); cover and digest at nearly boiling until melt is dissolved; remove crucible and cover, rinsing them carefully. Cool the solution and add 10

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[1] This correction of Al_2O_3 Fe_2O_3 for silica should not be made when the HFl correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 mg. of SiO_2 are still to be found with the Al_2O_3 Fe_2O_3.

[2] In this way only is the influence of titanium to be avoided and a correct result obtained from iron.

grams powdered C. P. zinc, No. 20. Let stand one hour, decant the liquid into a larger beaker, washing the zinc twice by decantation, and titrate at once with permanganate. Calculate the Fe_2O_3 and determine the Al_2O_3 by difference. Test Zn, etc., by a blank and deduct.

Notes.

Ferrous salts are oxidized by potassium permanganate in solutions containing free acid to ferric salts according to the reaction,

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Potassium permanganate does not give trustworthy results in the presence of free hydrochloric acid.

If the permanganate is prepared as directed above it is not changed very rapidly, provided it is kept in a dark place. It is well to standardize it occasionally, however.

To reduce the iron with hydrogen sulphide, place the solution into a flask and add to the solution one-tenth its volume of sulphuric acid and 25 cc. of strong hydrogen sulphide water. Heat to boiling. Now stopper the flask with a rubber stopper having two perforations through which two tubes pass. One tube should reach nearly to the bottom of the flask and the other just inside the stopper. Boil the solution until all hydrogen sulphide is expelled, passing carbon dioxide through the flask all the while, bringing it in through the long tube and out through the short one. The expulsion of the hydrogen sulphide may be tested by holding a piece of filter paper, moistened with lead acetate or nitrate solution, in the escaping steam from the short tube. As long as any hydrogen sulphide is present the paper is blackened or browned. The solution must be cooled in a current of carbon dioxide before titration with permanganate.

In dissolving the oxides of iron and aluminum in potassium bisulphate, the operation should be conducted at a low temperature, so as not to drive off the excess acid in the salt. The contents of the crucible should therefore be just hot enough to keep them fluid. The fusion with bisulphate is tedious, however, and until recently the writer determined ferric oxide in cement by the following methods. It is simpler than the above schemes and has the advantage of allowing a sample of one or two grams to be used for the determinations:

Weigh 1 gram of finely ground cement into a beaker and add 15 cc. of hydrochloric acid. Heat for ten to fifteen minutes, add 200 cc. of water and heat to boiling. Add ammonia in slight but distinct excess, boil a few minutes, allow the precipitate to settle, filter, using the filter pump if one is at hand, and wash two or three times with hot water. Place a clean flask under the funnel and redissolve the precipitate in a mixture of 15 cc. dilute sulphuric acid and 60 cc. water, made up in the beaker in which the precipitation was effected. Wash the filter and silica free from iron with cold water, pass through the reductor, described below, and titrate the solution with permanganate. Multiply the number of cubic centimeters of standard permanganate required by the ferric oxide value of the permanganate and then by 100. Divide the result by the weight of cement taken; the quotient will be the per cent. of ferric oxide, Fe_2O_3, in the cement.

The form of reductor best suited to cement work is the design of Dr. Porter W. Shimer, of Easton, Pa. His description of the apparatus[1] is as follows: "The reductor tube (Fig. 45) is a plain glass tube, three-eighths inch internal diameter, drawn out and cut off at its lower end. It is filled by placing a few small pieces of broken glass in the drawn-out portion, and on this about an inch of well cleaned sand. The tube is then filled with amalgamated zinc of as nearly uniform twenty mesh size as possible. About 80 grams are required. No asbestos or glass wool is used. The sand prevents particles of zinc from falling through and it does not become clogged by use. The consumption of zinc is very small, and when the column has settled about an inch a little fresh zinc can easily be poured in from above. The reductor tube is united with a 4-inch funnel by means of rubber tubing, well tightened with wire. Between the funnel and reductor is a Hoffman clamp. The lower end of the tube passes through a soft two-hole stopper so far as to reach half way to the bottom of a heavy-walled pint gas-bottle. The gas-bottle is connected with a filter pump through an intermediate safety bottle and valve. The funnel is clamped to a retort stand in such a

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[1] *Jour. Amer. Chem. Soc.*, XXI, 723.

manner as to allow the tube and gas bottle to swing easily in all directions. It is well to adjust the height so as to leave the gas bottle raised slightly above the base. The passage of the solution through the reductor may be effected either by use of the pump or by means of a vacuum obtained by condensation of steam, devised originally in Bunsen's laboratory. In using the latter method a little water may be boiled in the gas bottle until all air is expelled, and then quickly unite with the reductor, the clamp on the filter pump being closed. The speed of filtration is regulated by the upper clamp. Instead of filling the gas bottle with steam by boiling water in it, it is better to have a convenient tin or copper can containing boiling water and provided with one or more short steam outlet tubes on top. The empty gas bottle is inverted over one of these steam outlets and, when filled with live steam, is taken off and united as quickly as possible with the reductor. This latter method has the advantage of starting with an empty gas bottle which is desirable on the score of accuracy."

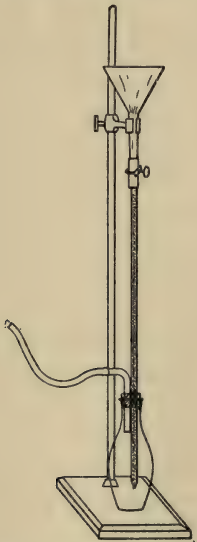

Fig. 45, Shimer's Reductor.

To use the reductor first pass, by the aid of suction, about 50 cc. of cold dilute sulphuric acid (1 part acid to 20 parts of water) through the reductor, and then follow with 200 cc. of cold distilled water. The Hoffman clamp should be closed before all the water has run out of the funnel so as to keep the tube full of water. Now empty the flask, again attach to the tube, pour the iron solution into the funnel and open the clamp. Just before the funnel becomes empty, run water around its sides and rinse the beaker well with water, running the washings also through the reductor, using about 100 to 150 cc. of water to wash the funnel and beaker. The time required for the iron solution to filter through the zinc, should be regulated by the upper clamp to occupy from three and a half to five minutes.

Instead of reducing the iron solution by means of a reductor, the gas bottle, mentioned on page 191, may be used. Pour the solution into the bottle. Add 1 gram of granulated zinc, stopper and allow to stand until the evolution of hydrogen slackens; then heat to boiling. When the zinc is completely dissolved (it may be necessary to add more acid to effect this), push down the glass tube, cool, and after adding 10 cc. of dilute sulphuric acid titrate with the permanganate.

The reduction may be accomplished with hydrogen sulphide also. The idea of the use of hydrogen sulphide is to do away with the error introduced by the presence of a small percentage of titanium, always found in cement. Titanium is reduced by zinc, and then oxidized by permanganate, causing the results for iron to be high. It is not reduced by hydrogen sulphide, hence the use of the latter. If the titanium is not determined and deducted from the alumina, however, the latter is too high, by just so much so that for practical purposes we might as well call titanium iron and use zinc as a reducing agent, as call it aluminum and use hydrogen sulphide.

By Titration with Potassium Bichromate. (Penny's Method).

Standard Potassium Bichromate.

Place from 10 to 15 grams of C. P. potassium bichromate in a sufficiently large platinum crucible. Heat carefully, avoiding all contact of the flame with the contents of the crucible, until the salt just fuses to a dark liquid. Then withdraw at once from the flame and let the crucible cool. Weigh 3.074 grams of the fused bichromate, which in cooling will have crumbled to a powder, dissolve in 250 to 300 cc. of cold water and pour into a liter graduated flask. Rinse out the beaker several times into the flask and dilute the solution to the liter mark. Mix well. One cc. of this solution should be equivalent to 0.005 gram of ferric oxide, Fe_2O_3.

To test or standardize the solution, weigh into a small beaker 0.4900 gram of pure ferrous ammonium sulphate (equivalent to 0.1 gram of ferric oxide). Dissolve in 50 cc. of water and, when all the salt is in solution, add 5 cc. of dilute hydrochloric acid. Run the bichromate solution from a burette into the liquid in the beaker until a drop of the iron solution placed upon a white porcelain plate and mixed by stirring with a drop of a freshly made 1 per cent. solution of potassium ferricyanide no longer assumes a blue color, but instead gives a yellow. This should require 20 cc. of the bichromate solution. If more or less, repeat the test, and if the first and second results agree, divide 0.1, the ferric oxide equivalent of the weight of the ferrous ammonium sulphate used, by the number of cubic centimeters of bichromate required. The result will give the ferric oxide equivalent, or value, in grams for each cubic centimeter of the standard potassium bichromate.

Some operators prefer to standardize their bichromate against iron wire. In this case clean 0.1 gram of fine iron wire by rubbing between fine emery paper and then between filter-paper. Coil around a lead pencil and weigh. Drop the coil in a small beaker, add 20 cc. of dilute hydrochloric acid and heat until all the wire dissolves. Wash down the sides of the beaker with a wash-bottle, bring the contents to a boil and drop in the stannous chloride solution, described below, slowly until the last drop turns the solution colorless. Remove from the source of heat and cool the liquid rapidly by setting the dish in a vessel of cold water. When nearly cold add at once 15 cc. of saturated mercuric chloride solution, and stir well. Allow to stand a few minutes and titrate with the bichromate as described above. Multiply the weight of the iron wire by 0.003 and deduct this from the original weight, for the impurities in the wire. The corrected weight divided by 0.7 and then by the number of cubic centimeters of bichromate required, gives the ferric oxide equivalent in grams to each cubic centimeter of the standard bichromate. This value should be checked unless within the limits of allowable error to 0.005 gram.

Stannous Chloride Solution.

Dissolve 100 grams of stannous chloride in a mixture of 300 cc. of water and 100 cc. of hydrochloric acid. Add scraps of metallic tin and boil until the solution is clear and colorless. Keep this solution in a closely stoppered bottle (best a dropping bottle) containing metallic tin. This solution should be kept from the air.

Mercuric Chloride Solution.

Make a saturated solution of mercuric chloride by putting an excess of the salt in a bottle and filling up with water and shaking as the solution gets low.

The Determination.

Weigh 1 gram of finely ground cement into a small beaker and add 15 cc. of dilute hydrochloric acid, heat from ten to fifteen minutes and add a little water. Heat to boiling and filter through a small filter, washing the residue well with water and catching the filtrate and washings in a porcelain dish. Add to the solution 5 cc. of dilute hydrochloric acid and bring to a boil. Add carefully, drop by drop, the stannous chloride solution until the last drop makes the solution colorless. Remove from the burner and cool the liquid by setting in a vessel of cold water. When nearly cold add 15 cc. of the mercuric chloride solution and stir the liquid in the dish with a glass rod. Allow the mixture to stand for a few minutes, during which time a slight white precipitate should form. Run in the standard bichromate solution carefully from a burette until a drop of the iron solution tested with a drop of 1 per cent. solution of potassium ferricyanide no longer shows a blue, but instead a yellow color. Multiply the number of cubic centimeters of bichromate used by the ferric oxide equivalent per cubic centimeter of the bichromate and divide the product by the weight of the sample. The result multiplied by 100 gives the per cent. of the ferric oxide, Fe_2O_3, in the cement.

Notes.

Treatment with hydrochloric acid is sufficient to dissolve all except a mere trace of iron in Portland cement.

A strongly acid solution of ferric chloride, if boiling hot, is instantly reduced to ferrous chloride by a solution of stannous chloride according to the following reaction:

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2$$

The operator can tell when complete reduction has taken place by the disappearance of the yellow color of the solution. The excess of stannous chloride is removed by addition of mercuric chloride when the following takes place:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

The precipitate, Hg_2Cl_2 should be white; if colored gray too much stannous chloride was used in reduction and mercury has been formed. As mercury reacts with the bichromate, when the precipitate formed on adding mercuric chloride is not perfectly white, but is colored gray, the determination should be repeated using more care to avoid a large excess of the tin solution. If no precipitate is formed on addition of mercuric chloride the stannous chloride has not been added in excess, and all the iron will not have been reduced to the ferrous state.

Ferrous salts are oxidized to ferric compounds by bichromate when in a solution containing a considerable excess of hydrochloric or sulphuric acid. The reaction is:

$$6FeCl_2+K_2Cr_2O_7+14HCl=3Fe_2Cl_6+Cr_2Cl_6+2KCl+7H_2O.$$

The ferrous ammonium sulphate has the formula $Fe(NH_4)_2(SO_4)_2.6H_2O$. It, therefore, contains one-seventh its weight of iron and is equivalent to 0.20408 of its weight of ferric oxide, Fe_2O_3. Fe_2O_3.

To make a 1 per cent. solution of potassium ferricyanide dissolve 1 gram of the salt in 100 cc. of water. Ferric compounds give a yellow color to this solution, while ferrous compounds impart an intense blue color. This solution must always be made up fresh as it is reduced by exposure to light.

The writer has experimented considerably with the above method during the past year, and he has found it thoroughly reliable. The presence of titanium does not affect its accuracy and a determination can easily be made in from 15 to 20 minutes.

DETERMINATION OF SULPHURIC ACID.

Gravimetric Method.

Weigh one gram of the sample into a small dry beaker and stir it up with 10 cc. of cold water until all lumps are broken up and the lighter particles are in suspension. Add 15 cc. of dilute (1-1) hydrochloric acid and heat until solution is complete. Filter through a small paper and wash the residue thoroughly. Dilute the filtrate to 250 cc., heat to boiling, and add 10 cc. of boiling 10 per cent. barium chloride solution. Stir well and allow to stand over night. Filter,[1] ignite, and weigh as $BaSO_4$, which multiplied by 0.34291 gives SO_3, or by 0.58565, gives calcium sulphate, $CaSO_4$. In this latter case multiply the percentage of calcium sulphate by 0.41185 and deduct from the percentage of lime for the true percentage of calcium oxide, CaO.

Photometric Method.

Jackson[1] has devised a rapid photometric method for determining sulphuric acid which is very convenient for checking this constituent in a large number of samples.

The apparatus[2] used in this method is shown in Fig. 46. Above is a glass tube closed at the bottom and graduated in millimeters depth. A convenient form of tube is a Nessler jar 2.5 cm. in diameter and 17 cm. to the 100 cc. mark. The brass holder for this tube is open at the bottom so that the glass tube rests on a narrow ring at this point. The candle below is so adjusted by means of a spring that the top edge is always just three inches below the bottom of the glass tube. The illustration shows the candle with the regulator cap removed so as to better represent the process. The English Standard Candle is preferred, but a common candle of the same size may be used. This candle must always be properly trimmed and the determination must be made rapidly so as not to heat the liquid to any extent. The most ac-

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[1] See Note, p. 206.

[2] Made by Baker & Fox, 83 Schermerhom St., Brooklyn, N, Y.

[1] *Chemical Engineer*, I., **6**, 361.

curate work is obtained in the dark room, and the candle should be so placed as not to be subjected to a draft of air. Care should be taken to keep the bottom of the tube clean both inside and out so as not to cut out any of the light.

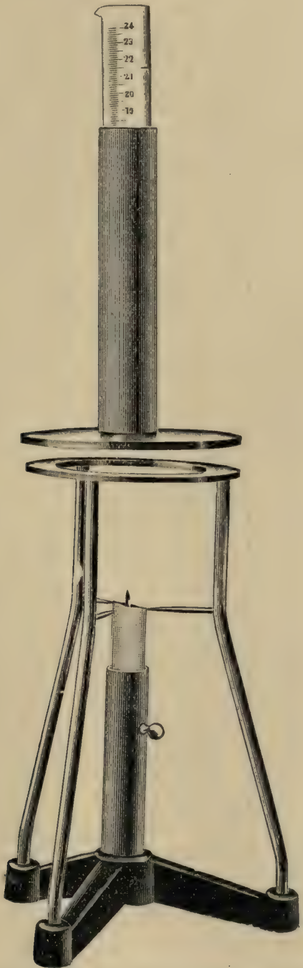

Fig. 46, Jackson's Apparatus for the Photometric Determination of Sulphates.

To determine the sulphate in a cement weigh out one gram, correct to centigrams, and rub up thoroughly with a glass rod in a small porcelain dish, or casserole, with two cubic centimeters of strong hydrochloric acid. Add about ten cubic centimeters of water and heat to boiling. Filter and wash with a small amount of hot water into a 100 cc. graduated Nessler jar, and fill with cold water nearly to the 100 cc. mark. If necessary suction may be employed in filtering, but usually a folded rib filter will do. Now add two grams of solid barium chloride crystals and make up to the 100 cc. mark with cold distilled water. Pour back and forth from the tube to a beaker until all of the barium chloride is dissolved. The solution is now ready for examination.

TABLE XXI.—FOR THE DETERMINATION OF SULPHATE IN CEMENT.

Depth cm.	Per cent. SO_3.	Depth Cm.	Per cent. SO_3.	Depth Cm.	Per cent. SO_3.	Depth Cm.	Per cent. SO_3.
1.0	5.2	4.0	1.4	7.0	0.8	10.0	0.6
1.1	4.8	4.1	1.4	7.1	0.8	10.2	0.6
1.2	4.4	4.2	1.3	7.2	0.8	10.4	0.6
1.3	4.1	4.3	1.3	7.3	0.8	10.6	0.5
1.4	3.8	4.4	1.3	7.4	0.8	10.8	0.5
1.5	3.6	4.5	1.3	7.5	0.8	11.0	0.5
1.6	3.4	4.6	1.2	7.6	0.8	11.2	0.5
1.7	3.2	4.7	1.2	7.7	0.7	11.4	0.5
1.8	3.0	4.8	1.2	7.8	0.7	11.6	0.5
1.9	2.9	4.9	1.2	7.9	0.7	11.8	0.5
2.0	2.7	5.0	1.1	8.0	0.7	12.0	0.5
2.1	2.6	5.1	1.1	8.1	0.7	12.2	0.5
2.2	2.5	5.2	1.1	8.2	0.7	12.4	0.5
2.3	2.4	5.3	1.1	8.3	0.7	12.6	0.5
2.4	2.3	5.4	1.0	8.4	0.7	12.8	0.4
2.5	2.2	5.5	1.0	8.5	0.7	13.0	0.4
2.6	2.1	5.6	1.0	8.6	0.7	13.5	0.4
2.7	2.1	5.7	1.0	8.7	0.7	14.0	0.4
2.8	2.0	5.8	1.0	8.8	0.6	14.5	0.4
2.9	1.9	5.9	1.0	8.9	0.6	15.0	0.4
3.0	1.9	6.0	0.9	9.0	0.6	15.5	0.4
3.1	1.8	6.1	0.9	9.1	0.6	16.0	0.4
3.2	1.7	6.2	0.9	9.2	0.6	16.5	0.4
3.3	1.7	6.3	0.9	9.3	0.6	17.0	0.3
3.4	1.6	6.4	0.9	9.4	0.6	17.5	0.3
3.5	1.6	6.5	0.9	9.5	0.6	18.0	0.3
3.6	1.6	6.6	0.9	9.6	0.6	18.5	0.3
3.7	1.5	6.7	0.8	9.7	0.6	19.0	0.3
3.8	1.5	6.8	0.8	9.8	0.6	19.5	0.3
3.9	1.4	6.9	0.8	9.9	0.6	20.0	0.3

The candle is trimmed and lighted; the solution is poured back and forth to get a thorough mixture of the precipitate of barium sulphate; and the glass tube is placed in position in the holder.

The liquid containing the precipitate is now poured into the graduated tube until the sight of the image of the flame of the candle is just visible. Then pour in a few drops at a time until it just disappears from view. The height to which this solution stands in the tube (reading the bottom of the meniscus) is then taken and from this reading the percentage of sulphates present in the cement may be read directly from the following table:

DETERMINATION OF TOTAL SULPHUR.

By Solution in HCl and Br.

Weigh one gram of the sample into a dry beaker and stir it up with 10 cc. of bromine water until all lumps are broken up and all except the heavier particles are in suspension. Add 15 cc. of dilute hydrochloric acid (1-1) and heat until solution is complete. Filter off the residue through a small filter and wash thoroughly with hot water. Dilute to 250 cc. and boil until all bromine is expelled. Now to the boiling solution add 10 cc. of 10 per cent. barium chloride solution, also boiling, and proceed as in the determination of sulphates.

By Fusion With Na_2CO_3 and KNO_3.

Place 1 gram of cement, finely ground and dried, in a large platinum crucible and thoroughly mix it by stirring with 6 grams of sodium carbonate and a little sodium or potassium nitrate.

Fuse the mixture, being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The heating of the crucible should be gradually done first over a Bunsen burner for a while and then over a blast lamp, until the contents of the crucible are in quiet fusion. Run the fused mass well up on the sides of the crucible and chill by dipping the bottom of the crucible in a vessel of cold water. If loose, remove the mass from the crucible to a beaker and cover with hot water. If not loose, fill the crucible with hot water and digest until the mass breaks up; then remove to the beaker. Cover the latter with a watch glass and acidify with hydrochloric acid. When effervescence ceases remove the watch glass, rinse into the dish and filter. Dilute the filtrate to 250 cc. and heat to boiling. Add 10 cc. of 10 per cent. barium chloride solution, also heated to boiling. Stir and heat for a few minutes and proceed as in the determination of sulphates.

DETERMINATION OF SULPHUR PRESENT AS CALCIUM SULPHIDE.

Weigh 5 grams of cement into a porcelain dish, and triturate with water until it shows no further tendency to set. Then wash out into the flask (Fig. 47) and cork tightly. Two-thirds fill the ten-inch test tube with a solution of lead oxide in caustic potash made by adding lead nitrate solution to potassium hydroxide solution (sp. gr. 1.27) until a permanent precipitate forms, and then filtering off the solution through asbestos after allowing the precipitate to settle. Run into the flask by means of the funnel 50 cc. of dilute hydrochloric acid and apply heat gently. Finally bring the acid to a boil and disconnect the delivery tube from the flask at the rubber joint. Collect the precipitate on a small filter, wash it once with water and then while still moist throw the precipitate and filter back into the test tube, in which has been placed some powdered potassium chlorate. Pour upon the filter and precipitate 10 cc. of concentrated hydrochloric acid. Allow to stand in a cool place until the fumes have passed off, then add 25 cc. of hot water, filter off the pulp, etc., and wash with hot water.

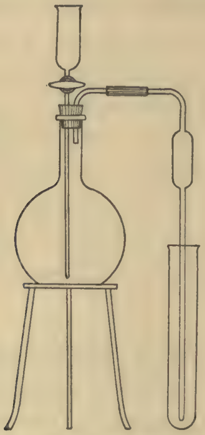

Fig. 47, Apparatus for Determining Sulphides.

Heat the filtrate to boiling and add ammonia until the solution is slightly alkaline. Then acidulate with a few drops of hydrochloric acid, add 10 cc. of a 10 per cent. solution of barium chloride, also brought to a boil, boil for a few minutes and stand in a cool place over night. Filter, wash, ignite, and weigh as barium sulphate. Multiply this weight by 0.30895 for calcium sulphide, CaS, or by 0.13734 for sulphur, S.

Notes.

Instead of alkaline lead nitrate solution, a solution of cadmium chloride made slightly alkaline with ammonia may be used to absorb the evolved hydrogen sulphide, in which case the cadmium sulphide precipitated, may be collected upon a previously weighed filter paper, dried, weighed and the sulphur calculated from this weight. For this method use 10 grams of cement for the sample and fill the test tube two-thirds full of a solution of cadmium chloride, made by dissolving 3 grams of cadmium chloride in 75 cc. of water, adding ammonia until the precipitate at first formed redissolves and then diluting to 500 cc. Proceed as usual. Collect the precipitate of cadmium sulphide upon a small counterpoised filter, or better in a Gooch crucible and felt, wash with water to which a little ammonia has been added, dry at 100° C., and weigh as cadmium sulphide, CdS. The weight of cadmium sulphide multiplied by 0.5000 gives the equivalent amount of calcium sulphide. Calculate the percentage and report as such or merely report as sulphur. If the former, calculate the total sulphur, as found by either of the methods on pages 59-60 to calcium sulphate, by multiplying the weight of the barium sulphate by 0.58565. Now multiply the percentage of calcium sulphate so found by 0.41185 and deduct the product from the percentage of lime (as found by precipitation as oxalate in the general scheme). The difference should be reported as calcium oxide, or lime, CaO. Multiply the percentage of calcium sulphide by 1.8872 for its equivalent in calcium sulphate and deduct from the percentage of total sulphur calculated as calcium sulphate. Report the difference as calcium sulphate.

Calcium sulphide may also be determined indirectly by determining first the sulphur present as sulphate and then the total sulphur. The difference will represent the sulphur present as sulphide. This may be reported either as CaS or as S. By this method, however, errors are made to appear as CaS.

Barium sulphate is a troublesome precipitate to filter as it is likely to run through the paper. For this reason it is well to use a double paper. Some operators use a Gooch[1] crucible, but a device suggested by Dr. Porter W. Shimer, of Easton, Pa., is still handier. It is shown in its simplest form in Fig. 48.[2] It consists of a glass tube cut off square at both ends, two inches long and one inch in internal diameter. The edges should be left sharp and not rounded in the flame. In the bottom of the tube is a rubber stopper fitted with a glass tube for attachment to the suction flask. On the stopper when inserted into the tube is a

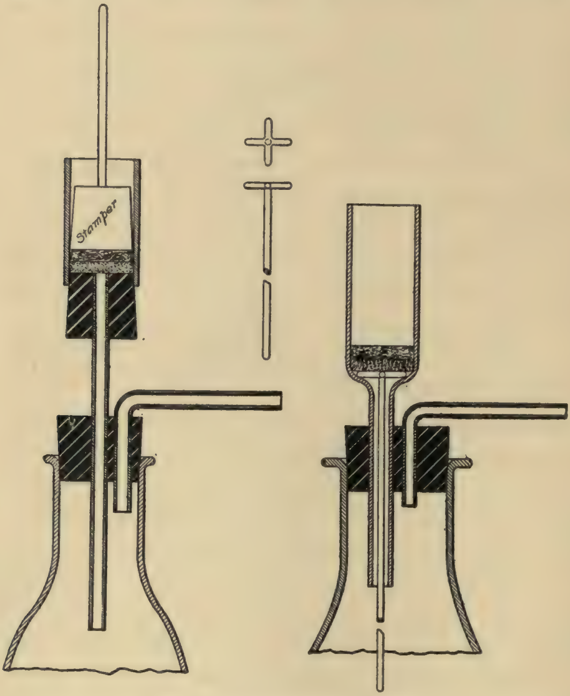

Fig. 48, Shimer's Filter Tube.

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[1] See page 184.

[2] *Jour. Amer. Chem. Soc.*, XXVII, 287. *Chemical Engineer*, II., 39.

disk of piano felt $^3/_{16}$ inch thick, fitting closely into the tube. The filter tube is now ready for the filter. Take unwashed Swedish filter paper, in any convenient amount, crush it into a ball in the hand and place it in a large cerecine hydrofluoric acid bottle from which the upper part has been cut. Add hydrochloric acid (sp. gr. 1.12 to 1.18) and a little hydrofluoric acid and stir vigorously with a paraffin-coated wooden stirrer until the paper has become a mass of fine soft pulp. Let it stand a few minutes and then add distilled water. In preparing a filter, pour some of this pulp in the beaker, dilute further with distilled water and pour enough on the felt, under suction, to make a filter of about ¼ inch. Compact this well by hard stamping with a stamper made from a solid rubber stopper, the larger end of which is only a little smaller than the inner diameter of the tube. A hole is made in the small end of the stopper, but not deep enough to pass quite through and a short glass rod inserted in this for a handle. Wash the filter two or three times with water and then filter off and wash the barium sulphate, using suction. This may be done rapidly without fear of a trace of the precipitate getting into the filtrate.

When filtration and washing are complete, turn off the suction and remove the filter tube from the stopper. Take the stamper and push the felt up until the filter projects beyond the tube, when the filter may be detached from the felt by a pair of forceps; or, if preferred, the upper end of the tube may be inserted into the weighed crucible and the felt and filter may be pushed at once into it, when the felt can be readily removed and the precipitate and filter ignited. Any precipitate adhering to the sides of the tube is taken along by the outgoing filter, for this reason the tube should be of uniform diameter, etc. The ash of these filters is less than that of an ordinary filter and the apparatus gives excellent results. It may, of course, be used for making other filtrations, but is particularly well adapted for use with barium sulphate.

It now seems to be pretty well established that it is not necessary to evaporate to dryness and separate silica, before precipitating sulphur with barium chloride, provided the solution is sufficiently dilute to guard against separation of gelatinous silica.

LOSS ON IGNITION.

Weigh 0.5 gram of cement into a weighed platinum crucible, cover with a lid, and heat for five minutes over a Bunsen burner, starting with a low flame and gradually raising it to its full height. Then heat for fifteen minutes over a blast lamp. Cool and weigh. The loss of weight represents the loss on ignition. This loss consists mainly of combined water and carbon dioxide driven off by the high temperature. Some chemists report, therefore, as "carbon dioxide and water," or having found the carbon dioxide subtract the percentage from that of the "loss on ignition" and call the remainder "water of combination" or combined water. As both sulphuric acid and alkalies are driven off, to some extent, at the temperature of the blast lamp, this is not strictly correct and it is best to merely report as "loss on ignition." This loss of alkalies is shown by the fact that if the crucible lid is rinsed off with distilled water, after the crucible has been ignited and weighed, and is then ignited for a moment to dry it and placed back on the crucible, the weight of the whole will be from 0.5 milligram to 1.5 milligram lighter, showing the condensation of the alkalies on the lid.

In conducting the ignition it is best to place the crucible with its bottom projecting through a round hole in a piece of platinum foil, which in turn rests upon a piece of asbestos board with a slightly larger hole cut in it. The flame should be played at an angle upon the bottom of the crucible so that the products of combustion are swept away from it.

DETERMINATION OF CARBON DIOXIDE AND COMBINED WATER.

Cements contain carbon dioxide, the amount varying from a mere trace in a fresh well-burned Portland cement to a large percentage in natural cements. Combined water is also present in cements, the amount varying as does the carbon dioxide with their age.

Apparatus.

For carrying out the determination of carbon dioxide and combined water at the same time, the apparatus designed by Dr. Porter W. Shimer, of Easton, Pa., for carbon combustions, is best suited.

The apparatus as used for carbon dioxide and combined water determinations is illustrated in Fig. 49. It consists of the following parts:

1. The aspirator bottles, *a′* and *a″*, the upper *a′*, filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. A potash bulb, *b*, containing a solution of caustic potash of 1.27 sp. gr. The form of bulb shown in the cut is Liebig's. Mohr's or any other form will do as well, but the Liebig bulb is the cheapest and answers as well here as the more expensive forms.

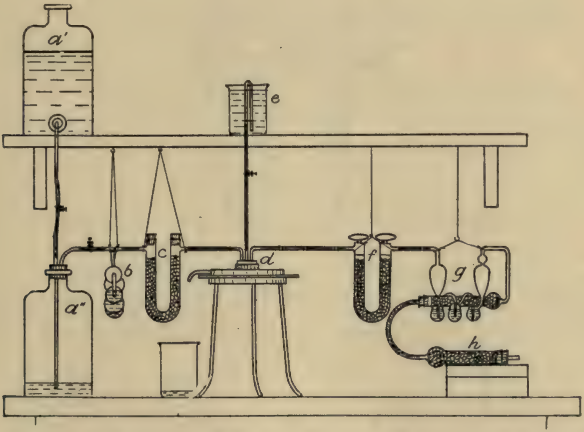

Fig. 49. Apparatus for Determining Carbon Dioxide and Water with Shimer's Crucible.

3. A **U**-tube, *c*, filled with dried granular calcium chloride. A straight calcium chloride tube may be used in place of the **U**-tube. It takes up more room, however.

4. A platinum crucible, *d*, provided with a water-jacketed stopper and reservoir, *e*, for supplying water to this latter. Fig. 50 shows the crucible stopper, etc., in detail. The water-cooled stopper is made of sheet copper, the joints being brazed. The stopper should be made as nearly perfectly circular as is possible, and free from indentations or imperfections in the brazing. The sides of

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[1] *Jour. Amer. Chem. Soc.*, XXI, 557 and XXIII., 227.

the stopper should not flare more than the sides of the crucible at the top. Too much flare has the tendency to cause the stopper to be forced out when under pressure. The stopper is somewhat smaller in diameter than the crucible opening, in order to allow space for a rubber band. This band may be obtained of stationers, and is of black rubber ¼ to ½ inch wide, and of sufficient length to stretch tightly around the lower part of the stopper. The crucible rests with its bottom through a circular opening in a piece of $^{3}/_{16}$ inch asbestos board which in turn rests upon a tripod.

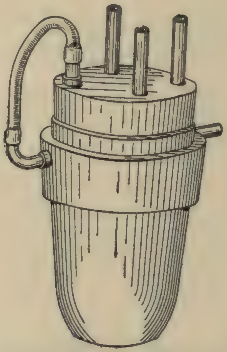

Fig. 50, Shimer's Water-Jacketed Crucible.

5. A small **U**-tube, *f*, filled with dried granular calcium chloride. The best form is that shown, provided with arms and glass stopcocks.

6. A potash bulb, *g*,with calcium chloride tube attached. The bulb should be filled with caustic potash of 1.27 specific gravity, and the tube with dried granular calcium chloride.

7. A guard tube, *h*, filled with dried granular calcium chloride.

Testing the Apparatus.

Fill the reservoir, *e*, with boiling water. Half fill the crucible with freshly ignited asbestos, and close it with the water-cooled stopper. A little powdered soapstone may be used as a lubricant. In putting in the stopper do not brace the thumb against the overflow tube, as this would risk bending the stopper at the base of the overflow. See that the apparatus is perfectly tight by running the aspirator and pinching the tube together just after the potash bulb.

Open the clamp and allow water to run out of the stopper. Place a Bunsen burner under the crucible. Open the clamp between the lower aspirator bottle and the potash bulb, *b,* and aspirate a current of air through the apparatus slowly for about twenty minutes. Detach the potash bulb, *g,* and the calcium chloride tube, *f,* and weigh. Again connect the bulb and tube in the train and aspirate air slowly through the apparatus for another twenty minutes. Detach the bulb, *g,* and tube, *f,* and again weigh them. This weight should agree to within 0.0005 of the former weight for the potash bulb, and 0.0003 for the calcium chloride tube. If not, after making sure there is no leakage in the apparatus, repeat the test. When the weights agree within the limits given, take the last pair as the weights of the bulb and tube, and proceed with the determination.

The Determination.

Weigh into the crucible from 1 to 3 grams of cement, cover with ignited asbestos stopper tightly. Test the apparatus and be sure there is no leakage. Place the Bunsen burner under the crucible after starting the hot water to flowing through the stopper. Cause a slow current of air from the aspirator bottle to flow through the apparatus. After ten minutes replace the Bunsen burner by a blast-lamp and continue the ignition for twenty minutes. Remove the lamp and aspirater air through the apparatus for ten minutes longer. Detach the potash bulb, *g,* and the calcium chloride tube, *f,* and weigh. The increase in weight of the former represents the carbon dioxide, CO_2, and of the latter water, H_2O.

Notes.

In this method the combined water and the carbon dioxide are driven out of the cement by ignition; the former is absorbed in a weighed calcium chloride tube and the latter in a weighed potash bulb. The increase in weight of the tube and bulb respectively represent the weight of combined water and carbon dioxide in the cement sample. The air entering the apparatus for the purpose of aspiration is purified of any water and carbon dioxide it is sure to contain by passing through the caustic potash and then over calcium chloride.

To make the upper aspirator bottle, bore a hole near the bottom of a five pint bottle with a file dipped in turpentine, and then slip into this hole a bit of glass tube covered with an inch or so of soft, thick-walled rubber tubing.

To fill the potash bulbs attach a short piece of rubber tubing to one end and dipping the other end in the caustic potash solution contained in a shallow dish apply suction to the rubber tubing with the mouth. When the bulbs are filled to the proper height (See Fig. 49) wipe the end dry inside and outside with pieces of filter paper.

Instead of the bulb, *b,* the air may be purified of any carbon dioxide it contains by causing it to bubble through caustic potash solution contained in two 4-ounce wide-mouthed bottles.

Calcium chloride sometimes, though not often, contains calcium oxide, which would absorb carbon dioxide. To saturate this, connect the apparatus, leaving out the potash bulb, *f,* and place a small piece of marble in the crucible. Now heat the crucible with a blast lamp and aspirate air slowly through the apparatus. Then take the marble out of the crucible and aspirate air for twenty minutes longer.

The potash bulbs and **U**-tube should be weighed as follows: Place the bulb upon one balance pan, and on the other the approximate weight. Stand the **U**-tube in the balance case. Close the door and do not open it for exactly twelve minutes. Then finish weighing the bulb so that the exact result is obtained in fifteen minutes from the time the bulb was placed on the pan. Now remove the bulb and weigh the **U**-tube quickly.

When not attached in the train the **U**-tube should have its stopcocks turned so as to close the openings, and the potash bulb should be "capped" with short pieces of rubber tubing containing, in one end, bits of capillary glass tubing.

If the cement should contain any appreciable quantity of carbonaceous matter, such as unburned coke, this would be burned to carbon dioxide causing high results. In this case first determine the carbon dioxide given off on ignition. Then weigh another sample into the crucible, add a little hydrochloric acid, filter off the residue on ignited asbestos, dry at 100° C, and determine the carbon dioxide in the residue as before. This will represent the carbon dioxide due to the burning of the organic matteer. The difference, of course, represents the carbon dioxide present in the cement as carbonate.

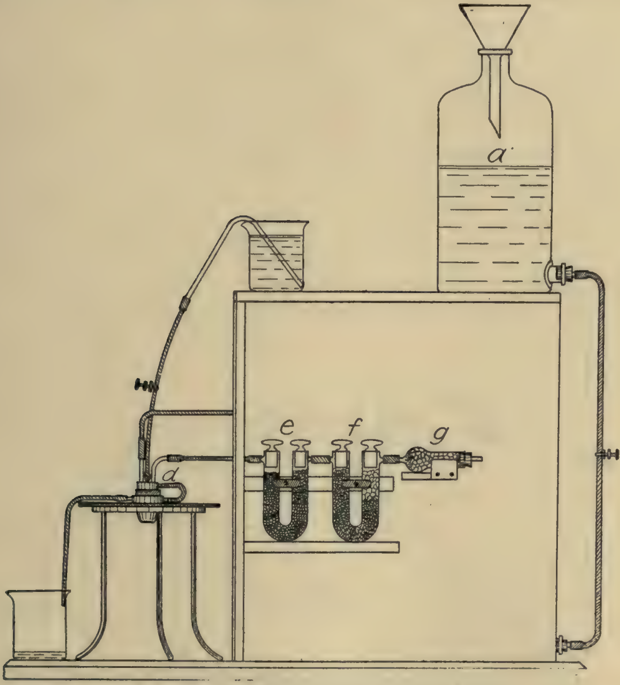

Fig. 51, Portable Apparatus for Carbon Dioxide and Water. Front.

A **U**-tube, containing soda-lime, may replace the potash bulb, *g*, This tube should be similar to *f*, and provided with ground glass stoppers. About an inch of calcium chloride should top the soda-lime in the limb next the guard tube, *h*.

When many carbon dioxide determinations have to be made, it will be found convenient to arrange the apparatus on a stand as shown in Figs. 51 and 52. Fig. 52 shows the front of the apparatus and Fig. 52 the reverse. The stand consists of a wooden base 1-1½ inches thick, and upon this is mounted an upright board. At the end of this board and running entirely across the base is fastened another upright at right angles to the first. These uprights support a shelf upon which rests the upper aspirator bottle and the reservoir for the water cooled stopper. The upright nearest the tripod should be protected against the heat of the blast lamp by covering with a sheet of asbestos. The **U**-tubes, etc., rest upon shelves as shown. The manner of clamping the **U**-tubes to the board is also shown in Fig. 53. *a'* and *a"* (Fig. 53) are aspirator bottles; *b* is filled with soda-lime and *c* with calcium chloride; *d* is Shimer's special form of water-jacketed platinum crucible; *e* (Fig. 50) is filled with calcium chloride, *f* with soda-lime topped with calcium chloride, and *g* with calcium chloride.

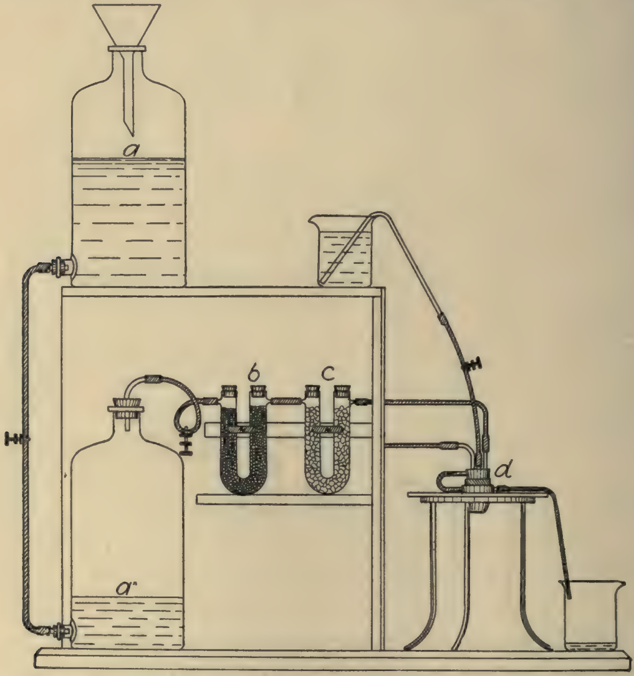

Fig. 52, Portable Apparatus for Carbon Dioxide and Water. Back.

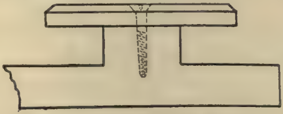

Fig. 53, Clamp for U-Tubes.

DETERMINATION OF CARBON DIOXIDE ALONE.

The apparatus just described for carbon dioxide and combined water determinations may, of course, be used for determining carbon dioxide only. In this case it is not necessary to weigh the calcium chloride tube, *f*, and in place of the expensive **U**-tube with its ground-glass stop-cocks, a simple straight form calcium chloride tube can be used just as well. Neither is it necessary to supply the stopper with hot water, and an empty potash bulb can replace the calcium chloride tube *c*. The determination is carried out precisely as if both the water and carbon dioxide were being considered, with, of course, the exception of not weighing the tube, *f*, at the end of the operation. If the stopper is wet with the finger before insertion into the crucible, it will be found to go in easier. This is, of course, not permissible when the water also is determined.

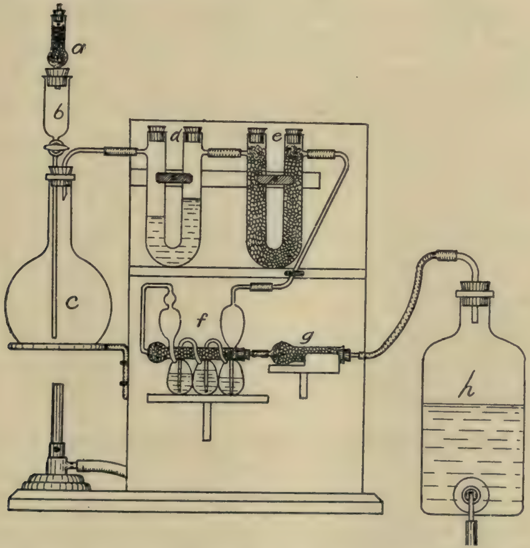

Fig. 54, Apparatus for Determining Carbon Dioxide by Evolution Method.

Some chemists prefer to determine carbon dioxide by liberating this constituent with hydrochloric acid and absorbing the evolved gas in a weighed potash bulb.

For carrying out the determination, refer to the apparatus (Fig. 49), for determining carbon dioxide and combined water.

Omit the **U**-tube, *c,* and substitute for the crucible, *d,* a 100 cc. wide-mouthed flask provided with a funnel tube. Follow the flask with a **U**-tube, containing sulphuric acid (sp. gr. 1.84) and this by the **U**-tube, *f,* the potash bulb, *g,* and the guard tube, *h.*

A convenient way of arranging the apparatus is shown in Fig. 54. *a* is filled with soda-lime; *b* is a funnel tube with ground-glass stop-cock; *c* the 100 cc. flask; *d* contains sulphuric acid; *e* and *g* calcium chloride; *f* is the weighed potash bulb, and *h* the aspirator bottle.

The Determination.

Weigh into the flask, *c,* from 2 to 10 grams of cement, triturate with water until all tendency to set has ceased, and connect the soda-lime tube *a* with the funnel tube. Aspirate a few liters of air through the apparatus, disconnect and weigh the potash bulb with its attached calcium chloride tube. Again connect the apparatus, aspirate another two liters, and again weigh the potash bulb and attached calcium chloride tube. If the first and second weights agree to within 0.0005 grams of each other, run into the flask 50 cc. of dilute hydrochloric acid and, if sulphides are present, a very little chromic acid. After connecting the bulb and tube in the train, and when action ceases apply heat gradually until the contents of the flask boil. Connect the soda-lime tube *a* and aspirate air slowly through the apparatus. Turn out the burner and aspirate two liters more of air. Disconnect the potash bulb and calcium chloride tube and weigh. The gain in weight is carbon dioxide. Divide the increase by the weight of the sample used and multiply the quotient by 100, for the percentage of carbon dioxide in the cement.

RAPID DETERMINATION OF CARBON DIOXIDE.

The Apparatus.

When rapid determinations of carbon dioxide have to be made, the following apparatus, which is a modification of Rose's form, may be used to advantage. It consists (Fig. 55) of a small 50 cc. Erlenmeyer flask, *a,* provided with a two-hole rubber stopper. Through one hole of this latter passes a 3-inch calcium chloride tube, *b,* and through the other a piece of bent glass tubing, *c,* one arm of which reaches nearly to the bottom of the flask, the other through another stopper to the bottom of a small wide tube, *d*. This latter is made from a 5-inch test tube. Such an apparatus will weigh from 35 to 60 grams according to the skill and choice of materials with which it is made.

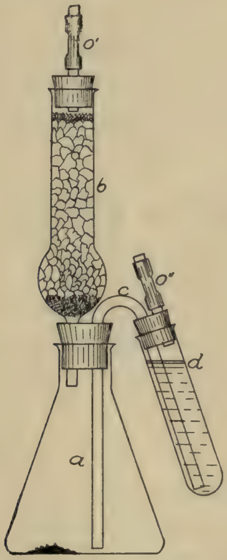

Fig. 55, Apparatus for Rapid Determination of Carbon Dioxide.

The Determination.

Place a little wool or cotton in the bottom of the calcium chloride tube and then fill the tube with calcium chloride. Next two-thirds fill the tube, *d*, with dilute hydrochloric acid, and weigh into the flask from 2 to 3 grams of Portland cement. Moisten the cement thoroughly with water, place the stopper in the flask, cap the openings, *o'* and *o''*, with pieces of rubber tubing closed at one end with bits of glass rod, and set in the balance case. After ten minutes weigh. Now attach a small guard tube, filled with calcium chloride, to the opening, *o'*, and after uncapping, *o''*, suck the acid from the tube, *d*, into the flask, *a*. As soon as the acid is all in *a*, close *o''* with the finger and cap quickly. Remove the guard tube, and after effervescence ceases place the apparatus on a hot plate until the contents of the flask begin to boil. Remove from the hot plate, cap the opening, *o′*, and set aside until the apparatus cools to the temperature of the room. Uncap *o″*, attach the guard tube to this opening this time, uncap *o′* and blow air gently through the apparatus for five to seven minutes. Cap the openings, place in the balance case, and after ten minutes weigh. Always, before weighing, uncap either *o′* or *o″* for a few seconds and then recap. This allows the pressure, caused by the change of temperature, to adjust itself. The loss in weight represents the carbon dioxide, CO_2, in the cement. Divide the loss by the weight of the sample and multiply the result by 100 for the percentage.

DETERMINATION OF HYGROSCOPIC WATER.

Weigh 5 grams of the sample upon a tared watch glass, spreading the former over the latter in a thin layer and dry for one hour, (or until it ceases to loose weight) at a temperature of 100°-110° C. Cool in a disiccator and weigh. The loss in weight represents "Hygroscopic Water" or "water below 110° C." or "H_2O-110°."

Notes.

Instead of a watch glass a weighed platinum or porcelain crucible may be used and a smaller sample (1 gram) taken.

Either of the two forms of air-bath described below will be found useful for drying the sample. The first can be procured of any dealer in chemical apparatus and the second can be made from "scraps" around the laboratory.

The ordinary air-bath consists of a copper box, provided with a hinged door in front, and holes for the insertion of thermometers and the escape of the water vapor, in its top. The box rests upon iron legs and is heated by a Bunsen burner underneath.

Air-baths are usually provided with false bottoms of sheet iron in order to prevent the destruction of the real one of copper by the burner flame. It is necessary to control the temperature of the air-bath by a thermometer inserted through a cork, in the opening, in the top of the oven. The required temperature can be maintained by adjusting the stop-cock of the gas supply. After the gas has once been regulated the temperature will remain constant for some hours. Gas regulators, called "thermostats," can be purchased from dealers in chemists' supplies, and while they are liable to become clogged and get out of order, they still are very convenient for keeping a constant temperature.

The author recently described (in the *Scientific American,* vol. lxxx, p. 230) a form of drying oven which he has used successfully in his laboratory for some years. It is non-corrosive, simple and cheap. In the metal ovens, the acid fumes, given off in "baking" certain substances, attack the metal, forming a scale which, in spite of care, will sooner or later drop in some sample or dish drying in the oven. Fig. 56 shows the oven. Select a large glass bottle and cut off the bottom by making a mark on it with a file, wrapping two strips of wet paper, one a little above and one a little below the mark, and revolving the bottle slowly and evenly while the tip of a small blowpipe flame or small flame from a blast lamp plays on the space between the paper. A crack will start in a few minutes, which will follow the flame around the bottle. The sharp edges should be smoothed by a file dipped

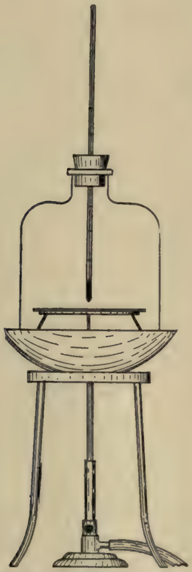

Fig. 56, Glass Drying Oven.

in turpentine, and a narrow strip of asbestos wound around the neck for a handle. The upper half of the bottle is placed upon a sand-bath or hot plate, and the object to be heated, upon a support of glass or porcelain, raised above the sand-bath by a wire bent to form a tripod. The temperature is regulated by a thermometer thrust through a cork in the mouth of the bottle. Large grooves should be cut lengthwise along the cork to make a free escape for the steam and vapors, and to create a current of hot air through the oven. Both this and the other form of air-bath described should be set in a corner shielded from air drafts. If this is done the maintaining of a constant temperature will be much simplified.

DETERMINATION OF ALKALIES.

J. Lawrence Smith's Method.

Mix 4 grams of the finely ground cement with 1 gram of ammonium chloride by grinding together in a clean agate mortar placed upon a sheet of black glazed paper. Add 4 grams of calcium carbonate free from alkalies, and transfer the mixture to a large platinum crucible provided with a closely-fitting cover. Heat gently at first, over a Bunsen burner, then gradually raise the temperature to a full red heat and keep so for an hour. Cool the crucible, and if loose, transfer the sintered mass to a small beaker or better a platinum dish. Wash the crucible and lid with hot water and pour into the dish or beaker. Digest the contents of the beaker until the sintered mass slakes to a fine powder.

If the sintered mass is not easily detached from the crucible, put the crucible into the beaker, add hot water and digest with heat until the mass slakes. Remove the crucible and wash it off into the beaker. Now filter into another platinum dish or beaker and wash the residue with water. Add 1.5 grams of pure ammonium carbonate, evaporate carefully to about 50 cc, and add a little more ammonium carbonate and a few drops of ammonia. Filter on a small filter into a dish of platinum or porcelain. Test the filtrate with a few drops of ammonium carbonate solution to make sure all the calcium has been precipitated. Evaporate to dryness and ignite at a barely visible red until all the ammonia salts are expelled and white fumes cease to come off. Cool, dissolve in a little water, add a few drops of barium chloride solution, and then a little ammonium carbonate solution and ammonium oxalate solution and ammonia, and filter from any residue that may form. Add three or four drops of dilute hydrochloric acid to the filtrate and evaporate to dryness in a weighed platinum dish. Ignite carefully as before and weigh as sodium chloride and potassium chloride, $NaCl + KCl$. Dissolve the mixed chlorides in water (they should be soluble without residue), and add to the solution an excess of platinic chloride solution. Evaporate nearly to dryness on the water-bath, add 20 cc. 80 per cent. alcohol and let stand until the sodium salts dissolve. Filter through a small filter and wash the precipitate by decantation with 80 per cent. alcohol, until the washings run through perfectly colorless. Dry the filter paper to drive off all the alcohol and then dissolve the small amount of precipitate on it by washing with hot water, allowing the washings to run into the weighed dish containing most of the potassium platinic chloride precipitate. Evaporate off the water. Dry at 135° C., and weigh as potassium platinic chloride, K_2PtCl_6. Multiply the weight by 0.19398 for potassium oxide, K_2O. To calculate the sodium oxide, multiply the weight of the potassium plantinic chloride by 0.30701 and subtract this from the weight of the residue of potassium and sodium chloride; the difference multiplied by 0.53076 gives the weight of the sodium oxide, Na_2O.

Notes.

During the first part of the incineration of the mixture of cement, calcium carbonate and ammonium chloride the heat should be kept low. The idea is not to volatilize the ammonium chloride, but to dissociate this into ammonia and hydrochloric acid by the heat. The latter then unites with the calcium carbonate to form calcium chloride.

If the dishes are removed direct from the water-bath to the flame for ignition decrepitation is sure to result. To guard against this place the dish in the air-bath at a temperature of 100° C. and gradually raise to 120° C., and then ignite over a moving flame.

The heating must not be too strong as potassium chloride is volatile. To test its freedom from ammonia salts, the residue of mixed chlorides, after weighing, should be again heated and weighed, to see if further loss occurs.

This operation should be repeated until the weights are constant.

DETERMINATION OF PHOSPHORIC ACID.

Weigh 5 grams of cement into a dry beaker and stir with 15 to 20 cc. of water until all lumps are broken up. Add from 30 to 50 cc. of hydrochloric acid (sp. gr. 1.20) cover with a watch-glass and heat until the cement is decomposed. Remove the cover, evaporate to hard dryness on the hot plate, and heat for from thirty minutes to one hour longer. Redissolve in 30 cc. of hydrochloric acid (sp. gr. 1.20) and evaporate to pasty consistency. Add 30 cc. of nitric acid (sp. gr. 1.42) and evaporate to 15 cc. Dilute with 30 cc. of water, heat, filter through a small filter and wash. Add ammonia until a slight precipitate forms, and then 3 cc. of concentrated nitric acid. The solution should now be amber-colored. Add 80 cc. of molybdate solution, heat to 80° C., and stir for five minutes. Let the solution stand one hour. Filter and wash well with acid ammonium sulphate solution. Dissolve the precipitate in the least possible quantity of dilute ammonia (1-5) and allow the solution to run into the beaker in which the precipitation was made. Wash the paper well with cold water. The filtrate should be clear and colorless. (If cloudy add hydrochloric acid until the liquid is acid, this usually precipitates the phosphomolybdate, then four or five drops of a concentrated solution of citric acid and finally ammonia until strongly alkaline). To the filtrate add slowly with constant stirring an excess of magnesia mixture. Stir for five minutes, then add one-third the volume of the solution of strong ammonia and allow to stand three or four hours. Filter, wash with a mixture of water 1000 cc., ammonia 500 cc., and ammonium nitrate 150 grams, dry, ignite, and weigh as $Mg_2P_2O_7$. To convert this weight to phosphorus pentoxide, P_2O_5, multiply by 0.63809.

Notes.

The solutions called for in the scheme are prepared in the following manner:

Molybdate Solution: Mix in a beaker 20 grams of pure molybdic acid with 80 cc. of cold distilled water and add 16 cc. of ammonia (sp. gr. 0.90). When solution is complete, filter and pour slowly into a mixture of 80 cc. of nitric acid and 120 cc. of water.

Ammonium Sulphate Solution: Add 15 cc. of ammonia (sp. gr. 0.90) to 1000 cc. of water and then 25 cc. of concentrated sulphuric acid (1.84 sp. gr.).

Magnesia Mixture: Dissolve 11 grams of crystallized magnesium chloride in water (or 2.2 grams of calcined magnesia in dilute hydrochloric acid avoiding an excess), filter, add 28 grams of ammonium chloride, 70 cc. of ammonia (sp. gr. 0.96), and enough water to make 200 cc. Filter before using.

DETERMINATION OF MANGANESE.

Colorimetric Method.

Stir 0.2 gram of cement with 10 cc. of water until all lumps are broken up, add 10 cc. of concentrated nitric acid and heat until solution is complete. Dilute to 100 cc., in a graduated flask, after cooling. Mix thoroughly and measure 10 cc. of this solution, into a small beaker, with a pipette. Add 2 cc. of nitric acid (1.2 sp. gr.) and heat to boiling. Remove from the flame and add 0.5 gram of lead peroxide, stir and boil for two minutes. Allow to stand some time and filter through a filter made of ignited, washed asbestos. The filtrate is caught in a graduated Nessler tube or cylinder and the filter is washed with a very little water. The solution and washings are then mixed. Into another cylinder from 1-3 cc. of a standard solution of manganese (made by dissolving 0.0556 gram of crystallized potassium permanganate in 500 cc. of water. Strength 1 cc. = 0.00005 gram MnO) is measured and the two cylinders stood side by side and viewed *horizontally*—not vertically. Water is then added to the standard to make it match the other tube. The height of the liquid in the two tubes is then read and the percentage of MnO calculated from the formula

$$X = \frac{a \times B \times 0.005}{A \times w}$$

When $a =$ number of cc. of standard solution placed in the cylinder and A the number of cc. to which it is diluted in order to produce the same shade as the cement sample diluted to B cc. W = weight of sample taken or 0.2 gram. It may be necessary where the cement is high in manganese to use a smaller sample than 0.2 gram.

DETERMINATION OF TITANIUM.

Colorimetric Method of A. Weller.

If titanium is to be determined, follow closely the method of analysis outlined on page 170. Purify the silica with hydrofluoric acid and ignite the iron and alumina precipitate in the same crucible with the residue from this treatment. Dissolve the precipitate, after weighing, in potassium bisulphate by fusion, and then the fused mass in water, acidified with sulphuric acid. Evaporate the fused mass until fumes of sulphuric acid come off. Dilute, filter and saturate the filtrate with hydrogen sulphide gas. Filter from any platinum sulphide and boil off the hydrogen sulphide in a current of carbon dioxide. Determine the iron by titration with potassium permanganate as described on page 192.

Concentrate the solution, after the titration is completed, to 50 cc. and transfer to a 50 cc. Nessler tube. Add 2 cc. of 3 per cent. hydrogen peroxide, absolutely free from fluorine. This produces an intense yellow color which is proportional to the amount of titanium present. Compare this color with that produced by hydrogen peroxide upon various volumes of a standard solution of titanium prepared as follows: Gently ignite potassium titanic fluoride and weigh 0.6000 grams of this into a platinum crucible. Add a little sulphuric acid and water, evaporate to dryness and expel the acid by gentle ignition. Repeat this process, and then dissolve in a little concentrated sulphuric acid and dilute to 200 cc. with 5 per cent. sulphuric acid. One cc. of this solution is equivalent to 0.001 gram of TiO_2 or to 0.2 per cent. when a half gram sample has been used. In comparing the colors measure into different tubes 0.5 cc., 1.0 cc., 1.5 cc., etc., portions of the standard titanium solution, dilute to the mark, and add 2 cc. of hydrogen peroxide to each. Compare with the color produced by the sample, making up new standards when the color lies between two of the above tubes, etc.

The method is accurate to about 0.01 per cent. when a one-half gram sample is taken.

CHAPTER X.

THE ANALYSIS OF CEMENT MIXTURES, SLURRY, Etc.

Since the success of cement-making depends primarily upon the proper portion of carbonate of lime to silica and alumina in the cement mixture, it is highly important to be able to rapidly estimate this ratio. If the materials from which the mixture is made are of normal constitution a determination in it of the calcium carbonate alone will suffice to check the correctness of the mixture.

For rapidly checking the percentage of calcium carbonate, two methods are in general use, the alkalimetric method in which the calcium carbonate is decomposed by a measured quantity of standard nitric or hydrochloric acid and the excess of acid determined by titration with standard alkali, and the indirect gas method in which the carbonate of lime is decomposed by acid and the evolved carbon dioxide gas collected in a suitable apparatus and measured; since the CO_2 is proportional to the $CaCO_3$,the percentage of lime can be calculated from the volume of CO_2. For the latter method the Scheibler's calcimeter is used. Neither of these methods gives very accurate results, and when the exact composition of the mixture is desired resort must be had to one of the longer gravimetric methods given further on.

When the slurry of the wet process is analyzed it should first be evaporated to dryness, then finely pulverized in a mortar and again dried for half an hour at 110° C. It will then be free from moisture and ready for analysis.

SAMPLING, ETC.

For the control of the composition of the mixture of raw materials it is usual to take samples at certain places during the grinding. In the dry process this is usually done either after the material leaves the ball mills, if these are used to do the grinding, or after the Griffin mills, if they are installed for this work. Where tube mills follow the ball mills it is usual to further check the composition of the raw material after it leaves these. The sample taken from any of the above sources will need further grinding but it is not usual to dry it, unless a complete analysis is to be made. Since either of the rapid schemes given below are affected by the fineness to which the sample is ground, it should be prepared the same way each time, usually by passing all of it through a 100-mesh test sieve. In the writer's laboratory the sample from the ball mills is taken by an automatic sampler which will be described further on, and brought to the laboratory in a small tin bucket. The sample is spread out on a piece of paper, after a thorough mixing by rolling back and forth on the paper, and divided into 15-20 squares with the point of a spatula. Two or three grams are taken from each of these squares and the main sample is then thrown away. The sample of from 50-100 grams is now made to pass a 100-mesh sieve, using a large wedgewood mortar to do the grinding. The finely ground sample is then mixed and 10-20 grams of it placed in a coin envelope or small bottle and taken to the chemical laboratory. The wedgewood mortar answers the purpose much better than an agate one would and, with the soft rock of the Lehigh District, does not contaminate the sample with silica to an amount which can be detected.

The following sampler, Fig. 57, was devised by the writer with the assistance of Mr. Owen Hess, Superintendent of the Dexter Portland Cement Co. It consists of a tin cone, of the dimensions shown, having a rectangular tin tube inserted at one point in its sides. The cone slips into a piece of four-inch pipe which in turn revolves in a rigid pillow block. The cone is revolved by the bevel gear arrangement shown, which is run from one of the mill shafts by a sprocket and chain, so as to make two or three revolutions per minute. The sampler is placed below an overhead screw conveyor carrying the ground material from the ball mills to the tube mill bins. A hole is cut in this conveyor trough, so that a stream of this material falls into the cone,, striking the side of the latter about 2 inches from the rim. As the cone revolves, the material falls into the cone and passes down through the hollow shaft into a pipe, which carries it back into the main elevator or one of the tube mill bins. When, however, the tube comes under the stream, it is deflected out of its course for a moment and passed through this tube down another pipe into a sample bucket placed at a convenient place. The frequency with which the sample is taken will depend on the number of revolutions per minute the cone makes. The amount will depend on the width of the inserted tube and the circumference of the cone. The sampler works well except when the raw material is *very* wet when the pipes clog up.

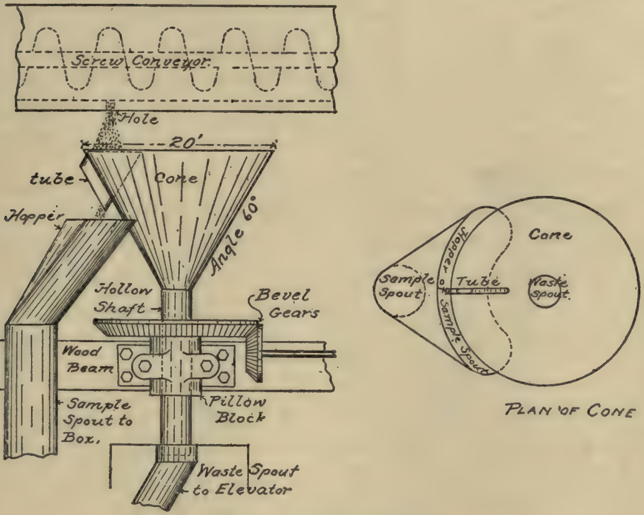

Fig. 57, Automatic Sampler.

In hand sampling from the ball mill, care must be taken not to get a false proportion of fine and coarse material in the sample. The best place to sample is from the conveyor leading from the mills, using a scoop made by tacking a piece of tin, three quarters of the way around, a piece of board 1½ inches square and 8 or 10 inches long as shown in Fig. 58. Never put the hand inside a screw conveyor while revolving, as loss of the member may result. A sample of cement rock-limestone mixture, after leaving the mills, will usually contain from 0.05 to 0.3 per cent. moisture. Even in wet weather when the dryer was being pushed to its

Fig. 58, Scoop for Sampler.

utmost and the mills were having trouble with the wet material I have seldom seen more than the latter figure present, so that for control and check purposes drying of the sample seems unnecessary.

In the wet process, the analytical methods for checking the composition of the slurry are practically the same as in the dry, but on the other hand, the sampling can not be done the same way and the sample itself must be freed from a large amount of water (50-60 per cent.) by drying. The slurry samples are usually taken from the mixing pits, and also after the slurry has passed through the tube mills, either from the discharge of the mill itself or else from the slurry pits.

The methods of sampling employed by the chemists at the various mills differ as the following will show:

Mr. W. H. Hitchcock, of the Egyptian Portland Cement Co., took samples from the mixing pit, by means of a pint cup, fastened to the end of a wooden pole by means of a wire. It is put in the slurry bottom side up, pushed down to the required depth, about the middle of the pit, and drawn up. As the pole is pulled, the cup rights itself and fills. Each pit holds 170 cu. yds. and is sampled in 20 places. The sample is then put in a miniature tube mill and ground for 10 minutes. From 25-35 grams of this sample are spread on a thin piece of cardboard and dried at 100% C., after which it is ground in an agate mortar when it is ready for the check determinations.

Mr. N. S. Potter, Jr., of the Peninsular Portland Cement Co., takes his sample from the slurry tanks, which are 16 ft. deep, by means of a two-quart tin pail, attached to the end of a pole by a common harness snap. The pail is pushed down into the slurry, bottom up, and full of air. At the desired point the pole is given a slight jerk when the pail rights, allow the air to escape and fills with the marl or slurry, as the case may be. The sample is then spread out on a piece of paper and dried on the hot plate.

Mr. Frank I. Post, of the Wolverine Portland Cement Co., uses a special form of sampler, consisting of a cup with two fly valves, one at the top and another at the bottom, attached to a pole. When the sampler is thrust down through the slurry, both valves open and the marl simply runs through the cup, but when the sampler is raised the valves shut, thus enclosing a sample in the cup. In removing this sampler from the tank care must be used not to lower it at all. If this is done, the valves of course, open and the sample previously taken is lost, and in its place will be a new sample from the point of lowering.

Mr. Homer C. Lask, of the Omega Portland Cement Co., also makes use of a bucket with a valve in sampling marl. His apparatus consists of a heavy iron bucket, three inches in diameter and nine or ten inches long. It has a valve in the bottom, which opens as the bucket sinks through the marl, but closes as soon as it is started in the opposite direction. A sample can thus be taken at any depth desired. The sampler is attached to a rope and sinks into the marl by its own weight. It is withdrawn by means of a small windlass. From three to five samples are taken from a tank, the different samples mixed together, and the whole taken as the tank sample.

The slurry is sampled, automatically, as it leaves the tube mill by an ingenious device. The tube mills at this plant have a central discharge and on the inner surface of the discharge conduit is attached a stout cup, of about 1 cu. in. capacity, with its open end towards the stream of slurry as the mill makes its revolution. The cup fills as it passes through the stream of slurry and discharges as it is carried over the top. A portion of the discharge is allowed to fall into a small trough, down which it flows into a bucket. This bucket holds about four pints and the sampler is so gauged that the former will fill in about an hour.

Samples of slurry and marl may also be taken by agitating the vat or tank thoroughly and then taking two or three small samples from the elevator or pump discharge and mixing and grinding. In order to correct the composition of slurry found to be under- or over-clayed, it is necessary to know not only how much carbonate of lime it contains, but also how much water. To determine the latter the usual rule is to evaporate a weighed portion of the slurry to dryness and determine the loss in weight. This evaporation can be carried on most rapidly and also safest in the "radiator." This consists of a round sheet iron box, with an open top and bottom flanged on. It is made of any convenient dimensions and usually with its diameter at the top a little larger than at the bottom. Convenient dimensions are 6 inches deep, 5½ inches diameter at the top and 4½ inches diameter at the bottom. The radiator will then set in the ring of a five-inch tripod. The substance to be evaporated is held on a triangle support, midway between the top and bottom of the box and made of heavy copper or iron wire. Fig. 59 shows the apparatus, which is to be heated by a burner.

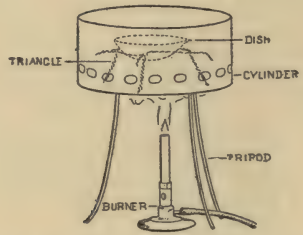

Fig. 59, Radiator for Drying Slurry Samples.

Practically the same results can be arrived at by using a round sheet iron cylinder, 6 inches high and 5 inches in diameter with a support 3 inches from the bottom, and setting over the hottest part of the hot plate. An ordinary porcelain dish may be made use of to hold the sample but a flat dish of tin or aluminum will serve the purpose better. Not only because greater surface is exposed but also because metal is a better conductor of heat than porcelain. As a quick test to determine when all the water is driven off, hold a cold watch glass over the dish and observe if any moisture collects on it. If 16.88 c.c. of slurry are taken for evaporation each 0.01 gram of dried residue will represent the number of pounds of dried slurry in a cubic yard of the wet slurry. This amount may be measured by means of a small pipette made to hold exactly this amount to the mark. In use the pipette must be washed out with a jet of water from a wash bottle. Or 168.8 c.c. may be taken when 0.1 gram will represent pounds per cu. yard, etc. When organic matter is present this also acts as a disturbing element in determining the correctness of the composition of the slurry. If constant, allowance can usually be made for it, but when variable the best plan is either to burn this off or else run the mix by a ratio of lime to insoluble.[1]

Mr. A. Lindteigen, of the Peerless Portland Cement Co., weighs the dried sample into a small iron tray, which is suspended in a larger one and this in its turn is covered and put over a good Bunsen burner for 20 minutes. In this way over three quarters of the organic matter is driven off without decomposing the carbonate. This also puts the sample in such a condition that it will sink in a solution of hydrochloric acid, and be quickly dissolved. Without this baking process the marl used by this company will float on top of the acid and even shaking and boiling will dissolve it only with difficulty. The baked sample, however, is very hygroscopic and takes up moisture rapidly from the air, so it must be weighed quickly.

RAPID METHODS FOR CHECKING THE PERCENTAGE OF CALCIUM CARBONATE IN CEMENT MIXTURES.

By Standard Acid and Alkali.

Phenolphthalein.

Dissolve 1 gram of phenolphthalein in 100 cc. of alcohol (50 per cent.). Keep in a small bottle provided with a perforated stopper through which passes a small pipette, made from a piece

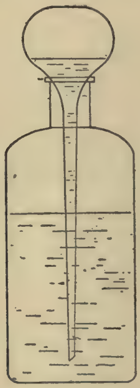

Fig. 60, Phenolphthalein Dropper.

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[1] See chapter IV.

of 5 inch narrow bore glass tubing by drawing out one end to a fine opening, and blowing a bulb in the other, Fig. 60.

One drop of this solution is sufficient for a determination.

Standard Alkali.

In order to prepare standard alkali of exactly $^2/_5$ N strength it is necessary to first prepare a standard solution of some acid, preferably of sulphuric, because of the ease with which this can be standardized by precipitation with barium chloride. To prepare this standard acid, measure out with a burette 11.2 cc. of concentrated sulphuric acid (1.84 sp. gr.) and dilute to one liter. Shake well and measure into each of two small beakers 10 cc. of this sulphuric acid and dilute to 100 cc. Add a few drops of hydrochloric acid, heat to boiling, and precipitate the sulphuric acid with barium chloride. Let the precipitate stand over night, then filter through a double filter (or preferably the Shimer filter[1]), wash with hot water, ignite and weigh. Calculate the quantity of this acid equivalent to 10 cc. of $^2/_5$N. sulphuric acid in the following manner. Ten cc. of $^2/_5$ N. sulphuric acid should give 0.467 grams of $BaSO_4$. If the average weight of both precipitates is *a* gram, then letting x represent the number of cubic centimeters containing 0.467 grams of $BaSO_4$,

$$0.467 : a :: x : 10 \text{ or } x = \frac{4.67}{a}$$

Hence $\frac{4.67}{a}$ cc. of our standard acid will be equivalent to 10 cc. of $^2/_5$ N. acid. This should be marked on the bottle and the solution put away in a dark cool place for use at some future time.

To prepare the standard alkali, dissolve 175 grams of caustic soda in eight liters of distilled water in a 2-gallon bottle (which usually holds 9 liters) and mix well by shaking. Now measure into each of two beakers the quantity of our standard sulphuric acid equivalent to 10 cc. of normal acid, and after adding a drop of phenolphthalein solution, run in the sodium hydroxide solution from a burette until the solution turns purple-red. The two titrations should check exactly. If not, repeat until they do. Now dilute the caustic soda solution so that it is exactly $^2/_5$ Normal.

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[1] See page 206.

The number of cubic centimeters of water necessary to add to the caustic soda solution may be found by the formula

$$\left(\frac{10}{b} - 1\right) \times C$$

when b = cc. soda required to neutralize the equivalent of 10 cc. of $^2/_5$ N. acid and C = quantity of caustic soda solution still left in the bottle.

Example of the preparation of the standard $^2/_5$ N. alkali.

Weight of 1st $BaSO_4$ precipitate	.4975
" " 2nd " "	.4987
Average	.4981

Therefore $\frac{4.670}{.4981} = 9.38$ cc. of the acid, are equivalent to 10 cc. of $^2/_5$ N acid.

Now 9.38 cc. of the above acid require 8.7 cc. of caustic soda, as determined by duplicate titrations. As we have used 20 cc. of our caustic soda we will have in the bottle 8000-20 = 7980 cc. and hence we must add to this $\left(\frac{10}{8.7} - 1\right)$7980 or 1189 cc. Since our bottle will only hold 9 liters it will probably be better to draw off exactly 1 litre when the amount to be added to the remainder will be $\left(\frac{10}{8.7} - 1\right)$6980 or 1040 cc. We therefore measure out this quantity and add it to the contents of the bottle.

The standard caustic soda solution should now be checked against the acid and, if not of correct strength, water must be added, as indicated, until it is exactly $^2/_5$ N. strength.

One cc. of this solution is equivalent to exactly 0.020 grams of $CaCO_3$, or 2.0 per cent. where a one gram sample is used. A two gallon bottle of standard alkali will make at least 2000 determinations so it pays to make it of correct strength and save calculations

Standard Acid.

Take the specific gravity of a bottle of hydrochloric acid, using a hydrometer for the purpose. Refer to the table of specific gravities of hydrochloric acid given below and calculate from this the quantity of acid necessary to contain 97.0 grams of HCl. Measure this quantity of the acid into a liter flask and dilute to the mark, pour into an eight liter bottle and add seven liters of water, measuring with the flask. Mix the contents of the bottle well by shaking. Ten cc. of this solution should be equivalent to from 8-1 to 8-5 cc. of the $^{2}/_{5}$ N. alkali when checked by adding a drop of phenolphthalein solution and running in the alkali to a purple-red color. If its value does not lie between these figures add acid or water to make it of this strength.

TABLE XXII.—SPECIFIC GRAVITIES OF HYDROCHLORIC ACID.

Sp. gr. at 15° C.	Degrees Baumé.	Degrees Twadd'l.	Per cent. of HCl.	Grams of HCl in 1 liter.	Correction of the sp. gr. for ± 1° C.
1.005	0.7	1	1.12	11.32	0.0006
1.010	1.4	2	2.12	21.45	0.0006
1.015	2.1	3	3.12	31.67	0.0006
1.020	2.7	4	4.11	41.99	0.0006
1.025	3.4	5	5.11	52.41	0.0006
1.030	4.1	6	6.11	62.93	0.0006
1.035	4.7	7	7.10	73.55	0.0006
1.040	5.4	8	8.10	84.27	0.0006
1.045	6.0	9	9.10	95.09	0.0006
1.050	6.7	10	10.09	106.01	0.0006
1.055	7.4	11	11.09	117.02	0.0006
1.060	8.0	12	12.09	128.14	0.0006
1.065	8.7	13	13.08	139.36	0.0006
1.070	9.4	14	14.08	150.68	0.0006
1.075	10.0	15	15.08	162.10	0.0006
1.080	10.6	16	16.07	173.63	0.0006
1.085	11.2	17	17.07	185.24	0.0006
1.090	11.9	18	18.07	196.96	0.0006
1.095	12.4	19	19.07	208.78	0.0006
1.100	13.0	20	20.06	220.70	0.0006
1.105	13.6	21	21.06	232.68	0.0006
1.110	14.2	22	22.06	244.80	0.0006
1.115	14.9	23	23.05	257.02	0.0006
1.120	15.4	24	24.05	269.34	0.0006
1.125	16.0	25	25.05	281.76	0.0006
1.130	16.5	26	26.04	294.28	0.0006
1.135	17.1	27	27.04	306.90	0.0006
1.140	17.7	28	28.04	319.62	0.0006
1.145	18.3	29	29.03	332.44	0.0006
1.150	18.8	30	30.03	345.36	0.0006
1.155	19.3	31	31.03	358.34	0.0006
1.160	19.8	32	32.02	371.44	0.0006
1.165	20.3	33	33.02	384.64	0.0006
1.170	20.9	34	34.02	397.94	0.0006
1.175	21.4	35	35.01	411.34	0.0006
1.180	22.0	36	36.01	424.84	0.0006
1.185	22.5	37	37.01	438.44	0.0006
1.190	23.0	38	38.01	452.14	0.0006
1.195	23.5	39	39.00	466.00	0.0006
1.200	24.0	40	40.00	479.84	0.0006

Example of the preparation of the standard acid.

On testing a bottle of hydrochloric acid its specific gravity is found to be 1.195° C. at 23° C. Correcting this to 15° C. we have $1.195 + (23 - 15) \times 0.0006 = 1.1998$, or practically 1.20 sp. gr. at 15° C. Hydrochloric acid of 1.20 sp. gr. contains 479.84 grams of HCl per litre or 0.480 grams per cubic centimeter. Therefore $\frac{97}{0.480}$ or 202 cc. will contain 97 grams of HCl, hence we measure out this quantity of acid and dilute to eight liters.

Standard Sample.

A standard sample of the raw material is necessary to standardize the acid and alkali for actual use. This sample should be ground in the same manner as the daily run of samples to be checked by the acid and alkali. It should all pass a 100-mesh sieve and be freed from hygroscopic moisture, by drying for some hours, at 110° C. Three or four pounds of this sample should be prepared and kept in air-tight jars or bottles. A small sample (one or two ounces) of this should be placed in a two ounce bottle and stoppered with a rubber cork when not in use. This small sample can then be re-dried for an hour at 100°-110° C. and used for standardizing, avoiding the frequent opening and mixing of the contents of the large jars or bottles.

After drying, the standard sample should be carefully analyzed. It should contain approximately the quantity of carbonate of lime which it is desired to have in the mix, and the amount of magnesia should also be normal. When the magnesia varies at different times fresh standard samples should be prepared to contain these varying percentages of magnesia; otherwise the lime will be reported too high.

Standardizing the Acid.

Weigh one gram of the standard sample into a 600 cc.Erlenmeyer flask and run in from a pipette 50 cc. of standard acid. Close the flask with a rubber stopper, having inserted through it a long glass tube 30 inches long and about ⅜-inch internal diameter. Heat the flask on a wire gauze over a burner as shown in Fig. 61 until steam *just begins* to escape from the upper end of the tube. The heating should be so regulated, that the operation requires very nearly two minutes, from the time the heat is applied, until steam issues from the tube. Remove the flask from the heat, as soon as the steam escapes from the tube, and rinse the tube into the flask, in the following manner. Rest the flask, still stoppered, on the table and grasp the tube between the thumb and forefinger of the left hand. Direct a stream of cold water, from a wash bottle in the right hand, down the tube, holding the latter inclined at an angle of 45°, and rolling the flask from side to side on the table, in sweeps of two or three feet, by twirling the tube between the finger and thumb. Unstopper the flask and rinse off the sides and bottom of the stopper, into the flask, and wash down the sides of the latter. Add a drop or two of phenolphthalein and run in the standard alkali, from a burette, until the color changes to purple-red. This color is often obscured until the organic matter settles, so it is necessary to hold the flask to the light and observe the change by glancing across the surface. A little practice will easily enable the operator to carry on the titration with accuracy and precision.

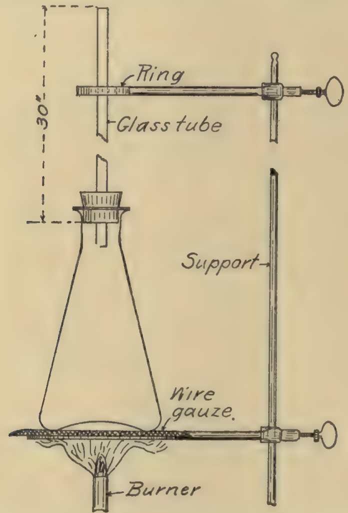

Fig. 61, Apparatus for Determining Calcium Carbonate with Acid and Alkali.

If the standard sample contains L per cent. carbonate of lime and d cc. of alkali are required to produce the purple-red color, then to find the carbonate of lime in other samples it is only necessary to subtract the number of cubic centimeters of alkali required in their case from *d*, multiply the difference by 2 and add to *L* for the percentage of carbonate of lime in them; or if the number of cc. is greater than *d*, subtract *d* from this number, multiply by 2 and subtract from *L* for the carbonate of lime.

In order to avoid all calculations prepare a table giving the various percentages of carbonate of lime corresponding to different quantities of alkali.

Example of Such a Table: Suppose the standard sample contains 75.0 per cent. carbonate of lime and 4.6 cc. of standard alkali are required to produce a purple-red color. Then since each cc. of alkali is equivalent to 0.02 grams or 2 per cent. of carbonate of lime 4.5 cc. alkali would represent 75.2 per cent. carbonate of lime and 4.4 cc. alkali would be equivalent to 75.4 per cent. carbonate of lime. Similarly 4.7 cc. alkali are equal to 74.8 per cent. carbonate of lime. So we see the lime progresses by 0.2 per cent. for each decrease of 0.1 cc. alkali and we can quickly write the following table:

cc. Alkali.	Per cent. $CaCO_3$.	cc. Alkali.	Per cent. $CaCO_3$.	cc. Alkali.	Per cent. $CaCO_3$.
3.8	76.6	4.5	75.0	5.2	73.8
3.85	76.5	4.55	75.1	5.25	73.7
3.9	76.4	4.6	75.0	5.3	73.6
3.95	76.3	4.65	74.9	5.35	73.5
4.0	76.2	4.7	74.8	5.4	73.4
4.05	76.1	4.75	74.7	5.45	73.3
4.1	76.0	4.8	74.6	5.5	73.2
4.15	75.9	4.85	74.5	5.55	73.1
4.2	75.8	4.9	74.4	5.6	73.0
4.25	75.7	4.95	74.3	5.65	72.9
4.3	75.6	5.0	74.2	5.7	72.8
4.35	75.5	5.0	74.1	5.75	72.7
4.4	75.4	5.1	74.0	5.8	72.6
4.45	75.3	5.15	73.9	5.85	72.5

Determination.

Weigh 1 gram of the sample, which has been ground to pass a 100-mesh sieve, into the flask, add 50 cc. of the standard acid and proceed as directed under standardizing the acid. The percentage of carbonate of lime may be found from the number of cc. of alkali used either from the preceding table or by the formula

$$\%\ CaCO_3 = L - (d - S) \times 2$$

Where *L* and *d* have the same values as in the paragraph on "Standardizing the Acid" and *S* represents the number of cubic centimeters required for the sample whose composition is desired. If 4.25 cc. of alkali are required then the sample contains $75 - (4.6 - 4.25) \times 2 = 75.7$ per cent. carbonate of lime.

NOTES.

The process depends upon the decomposition of calcium carbonate by a measured quantity of standard alkali in excess of that required by theory and then determining the excess acid by titration with standard alkali.

$$\underset{100.1}{CaCO_3} + \underset{36.45}{2HCl} = CaCl_2 + H_2O + CO_2$$

$$\underset{36.45}{HCl} + \underset{40.05}{NaOH} = NaCl + H_2O$$

Hence, 1 cc. of $^2/_5$ normal acid will decompose 0.02 grams of $CaCO_3$ and 1 cc. of $^2/_5$ normal acid will neutralize as much acid as 0.02 grams of $CaCO_3$.

Phenolphthalein is a very delicate indicator. It is, however, very susceptible to carbon dioxide and the solution must be freed from the latter by boiling whenever this indicator is used. It is also useless in the presence of free ammonia or its compounds. The addition of a few drops of the indicator to an acid or neutral solution shows no color, but the faintest excess of caustic alkali gives a sudden change to purple-red. Methyl orange may be used in place of phenolphthalein. While not so delicate it possesses certain advantages over the latter. It can be used in the cold with carbonates, and its delicacy is not impaired by the presence of ammonia or its salts. A convenient strength for the methyl-orange indicator is 0.1 gram of the salt to 100 cc. of water. One drop of this solution is sufficient for 100 cc. of any colorless solution. Alkaline liquids are faintly yellow with methyl-orange and acid ones are pink. Of the two indicators, however, phenolphthalein is much to be preferred for this work, as the carbon dioxide has all been boiled off the acid and provided the alkali is properly kept, the amount in this is constant and hence exercises the same influence all the time.

Standard $^2/_5$ N caustic soda may be prepared, however, free from carbon dioxide, by the following method: Take about twice the quantity of caustic soda required for the standard solution, dissolve in water and add 25 grams of freshly slaked lime made into a milky paste with water. Boil for 10 or 15 minutes and, when cool enough to avoid cracking the latter, pour into a five-pint bottle. Add water enough to nearly fill the bottle, stopper, shake and let stand over night to settle. In the morning, siphon off the clear liquid and make up to five or six liters. Run against the standard sulphuric acid solution and dilute as directed above for the preparation of $^2/_5$ N alkali.

As a preliminary standard for the preparation of the $^2/_5$ N alkali, hydrochloric acid may be used instead of sulphuric acid. It is more troublesome to standardize, however. Prepare the $^2/_5$ normal hydrochloric acid as directed in the scheme and standardize gravimetrically as follows:

To any convenient quantity of the acid to be standardized, add solution of silver nitrate in slight excess, and 2 cc. pure nitric acid (sp. gr. 1.2). Heat to boiling point, and keep at this temperature for some minutes without allowing violent ebullition, and with constant stirring, until the precipitate assumes the granular form. Allow to cool somewhat, and then filter through asbestos. Wash the precipitate by decantation, with 200 cc. of very hot water, to which has been added 8 cc. of nitric acid and 2 cc. of dilute solution of silver nitrate containing 1 gram of the salt in 100 cc. of water. The washing by decantation is performed by adding the hot mixture in small quantities at a time, beating up the precipitate well with a thin glass rod after each addition. The pump is kept in action all the time; but to keep out dust during the washing, the cover is only removed from the crucible when the fluid is to be added.

Put the vessels containing the precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove from the receiver, and set aside to recover the silver. Rinse the receiver and complete the washing of the precipitate with about 200 cc. of cold water. Half of this is used to wash by decantation and the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chloride being broken down with a glass rod. Remove the second filtrate from the receiver and pass about 20 cc. of alcohol (98 per cent.) through the precipitate. Dry at from 140° to 150°. Exposure for half an hour is found more than sufficient at this temperature, to dry the precipitate thoroughly. The weight of silver chloride multiplied by 0.25424 gives the hydrochloric acid in the volume taken.

Instead of $^2/_5$ normal caustic soda the corresponding $^2/_5$ normal caustic potash may be used. To prepare, substitute 220 grams of KOH for 175 grams of NaOH, and proceed as directed in the scheme.

The standard hydrochloric acid used in the determination itself is not exactly $^2/_5$ normal; in fact, is much weaker than this. It is made so in order to avoid waste of the alkali. If made $^2/_5$ normal strength, it would require about 12.5 cc. of alkali to titrate back. A smaller pipette might be used or the acid measured with a burette. The automatic pipettes are usually made in sizes, 25 cc., 50 cc., etc., and are so convenient for measuring the acid that, as there is nothing to be gained by making the acid $^2/_5$ normal strength, it will be found more convenient to make it of the strength indicated in the scheme, and use a 50 cc. automatic pipette.

In some laboratories, the acid and alkali are both made of $^1/_5$ N strength and a half gram sample is used for the determination. There appears to be nothing gained by this and something may be lost as the stronger acid is a better solvent for the sample.

The bottle of strong hydrochloric acid, used to make the standard acid, should be marked with the number of cubic centimeters required to make eight liters of standard acid and put away for use in making up the next lot of acid.

In preparing a second lot of acid it will save calculation and the preparation of a new table, if the acid is made up to the same strength as before. To do this make a little weaker than the figures call for and ascertain its strength by a trial determination on the standard sample, then, if too much carbonate of lime is found, add acid cautiously until the value of a determination made with the standard sample shows the proper percentage of lime.

Standard nitric acid may be used in place of the standard hydrochloric acid. It keeps better and is not quite so volatile, but, on the other hand, is not so good a solvent. On the cement rock mixtures of the Lehigh District hydrochloric acid works best, but nitric acid is used in the laboratories of several of the wet process mills in the west. The nitric acid is prepared exactly as the hydrochloric acid, using such a quantity of strong acid, however, as will contain 167 grams of HNO_3.

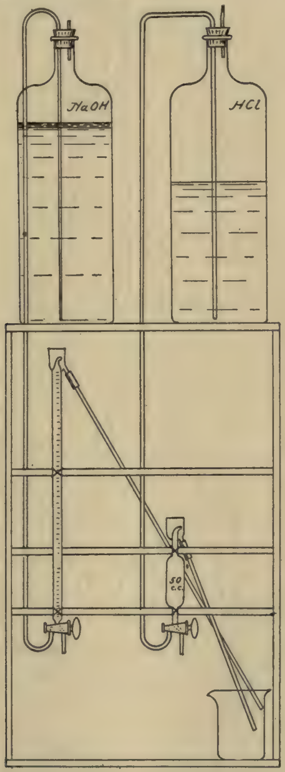

Fig. 62, Standard for Acid and Alkali Bottles and Pipettes.

The object of the long glass tube is that of a condenser to catch any volatilized acid. This may be replaced by a Leibig's return condenser cooled by water or by a tube full of glass beads, which are wet before the determination with cold distilled water.

Fig. 62 shows a convenient way of arranging the bottles, burettes and pipette for the acid and alkali. Its construction is so evident from the drawing that a description seems unnecessary. Both the burette and pipette are of the Eimer and Amend automatic zero point pattern. Fig. 63 shows the pipette in detail.

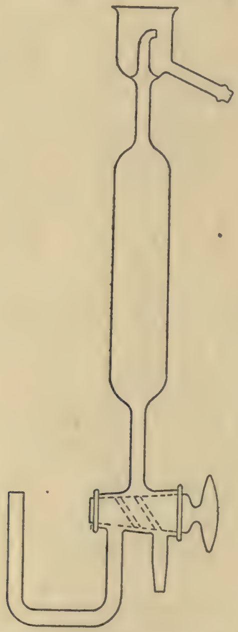

Fig. 63, Automatic Pipette.

A perpetual table for use with any strength acid and alkali may be made as follows: The number of cubic centimeters and twentieths cubic centimeter of alkali from 3 to 8 are written on a piece of stiff paper and pasted fast to a soft pine board. The percentages and tenths of carbonate of lime from 70 to 78 are next written on a piece of cardboard and this is merely fastened to the board with thumb tacks so that the number of cubic centimeters of acid required by the standard sample coincide with the percentage of lime it contains. For instance, in the example given 75 per cent. lime are made to coincide with 4.6 cc. of alkali. The board is then to be hung up on the wall behind the alkali burette, etc.

By Scheibler's Calcimeter.

Apparatus.

Fig. 64 shows the form of the calcimeter. It consists of the following parts:

1. A small bottle, A, provided with a perforated stopper. In the bottle is placed a tube, *s*, of gutta-percha or glass.

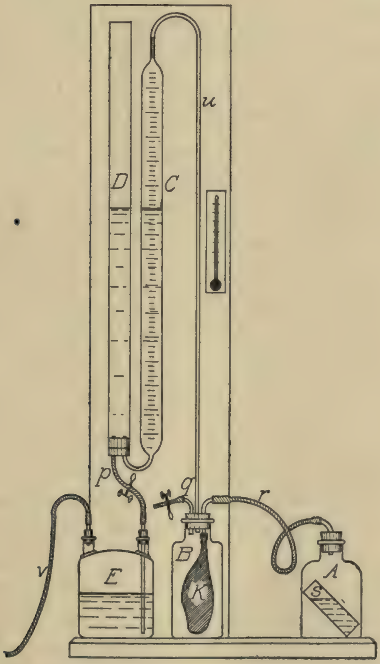

Fig. 64, Scheibler's Calcimeter.

2. Another bottle, B, provided with three openings in its neck. The right hand opening of the bottle contains a firmly fixed glass tube which connects, on the one end with A by means of the flexible rubber tube, *r*, and on the other, inside of the bottle, B, with a very thin India-rubber bladder, K. The left hand opening is

controlled by a pinch-cock on a piece of rubber tubing slipped over the glass tube, *q*. The central opening connects B with the measuring tube.

3. An accurately graduated glass cylinder, C, of about 150 cc. capacity.

4. Another glass cylinder, D, serving to regulate the pressure of the gas measured in C.

5. A water reservoir, E, consisting of a two-necked Woulff bottle. A glass tube, *p*, passes through a stopper in one neck nearly to the bottom of the reservoir and is connected with D by means of a piece of rubber tubing. The communication between D and E is controlled by means of a spring clamp.

The whole apparatus with the exception of the first bottle, A, is fastened to a suitable stand by means of brass fittings and a thermometer is also attached.

Open the spring clamp, *p*, and pour distilled water into D by means of a funnel until the bottle, E, is nearly full. When ready for a determination, remove the stopper from A, open the spring clamp, *p*, and blow air into *v* from the mouth until the level of the water in C and D reaches the zero point in the former. Care should be taken not to blow the water into the tube, *u*. If the level of the water passes the zero mark on C, it may be brought to the proper point by opening the spring clamp, *p*. The level in both tubes should be the same and stand exactly at the zero mark in C. The filling of the tube, C, will cause the bladder, K, to empty. If this does not happen, open the clamp, *q*, and blow air into B until the bladder flattens. If K is exhausted before C is filled the water in this latter tube will stand below that in D; in this case also open *q* until the levels are the same and at the zero point in C.

The Determination.

Place in the bottle, A, a weighed quantity of the dried slurry, cement mixture or limestone, in a finely powdered condition. Fill the cup, *s*, with 10 cc. of dilute (1 : 1) hydrochloric acid and place cautiously in A taking care not to spill any of the acid into the bottle. Stopper A tightly, greasing the glass stopper with a little tallow. This will cause the water in C to sink and in D to rise a little. Open q until the levels are the same, close and note the thermometer and barometer reading. Raise the bottle and tilt it slightly so that the acid in s runs into A, and gradually mixes with the sample. In doing this hold the bottle by the neck, to avoid warming, with the right hand and at the same time regulate p with the left so that the water in the two tubes is kept at the same height. Continue this operation until the water in C does not change its level for a few seconds. Now bring the columns of water in C and D to the same level and take the height in the tube, C, and note the reading of the thermometer to see if the temperature has remained constant.

Calculation of Results.

It is necessary as the first step to calculating the weight of calcium oxide equivalent to the volume of gas gives off, to correct such volume for temperature, pressure, the tension of aqueous vapor and the gas absorbed or held back by the hydrochloric acid. This latter amounts to 7 per cent. of the volume given off.[1] To make the necessary corrections use the formula

$$V = v \times \frac{100}{93} \times \left(\frac{1}{1 + 0.00367\,t} \times \frac{p - s}{760}\right)$$

in which

$V =$ corrected volume (in cc)
$v =$ uncorrected volume (in cc.)
$t =$ temperature, C°
$p =$ pressure, mm. of mercury
$s =$ tension of aqueous vapor at t° C. as given in the table on page 98.

To find the weight of V cc. of carbon dioxide, multiply V by 0.0019712, the weight of 1 cc. of carbon dioxide, when measured at 0° C. and 760 mm. of mercury pressure. To convert this weight of carbon dioxide to its equivalent of lime, CaO, multiply this latter result by 1.2743; or to convert to calcium carbonate, $CaCO_3$, multiply by 2,2743.

$$\text{Or : Weight of CaO} = 0.002689 \times v \left(\frac{1}{1 + 00467\,t} \times \frac{p - s}{760}\right)$$

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[1] Warrington, *Chemical News*, XXXI., 253.

TABLE XXIII.—TENSION OF AQUEOUS VAPOR.

t. Temp. °C.	*s.* Tension in mm. of mercury.	*t.* Temp. °C.	*s.* Tension in mm of mercury.	*t.* Temp. °C.	*s.* Tension in mm. of mercury.
10	9.2	18	15.4	26	25.0
11	9.8	19	16.3	27	26.5
12	10.5	20	17.4	28	28.1
13	11.2	21	18.5	29	29.8
14	11.9	22	19.7	30	31.6
15	12.7	23	20.9	31	33.4
16	13.5	24	22.2	32	35.4
17	14.4	25	23.5	33	37.4

Notes.

Tables are usually sold with these instruments which very much shorten the calculations, a graphic table such as the author describes in his "Chemists' Pocket Manual" would greatly simplify the calculations necessary with this instrument.

The above corrections for the volume of carbon dioxide may be done away with, by making a determination either with a standard sample of slurry or cement mixture or with pure calcium carbonate (Iceland spar) before each series of experiments with this instrument. If the temperature and pressure remain the same during the time for the series the result with the standard sample will give the relation between the volume of carbon dioxide and the weight of lime. For example, 0.5 gram of finely powdered Iceland spar ($CaCO_3$) was weighed out and the volume of carbon dioxide then measured and found to be 111.5 cc. 0.7 gram of the slurry, whose percentage of lime is desired, was next weighed out and the volume of gas found to be 116.5 cc. Now 0.5 gram of calcium carbonate is equivalent to 0.28 gram of lime. Then, volume of gas given off by the Iceland spar: that given off by the slurry:: weight of lime in Iceland spar: that in the slurry; or 111.5: 116.5:: 0.28: x from which $x = 0.2927$, and per cent. of lime in slurry $= \frac{0.2927 \times 100}{0.7} = 41.81.$

The apparatus should be placed where direct sunlight cannot fall upon it, and also be protected from any heating apparatus, such as radiator or stove, or Bunsen burner. It should also be stood near a north window so as to have sufficient light for reading and adjusting the water levels.

The Dietrich, Faija and Marshall calcimeters are all improvements upon the Scheibler apparatus. The latter is probably the best of the three and is described in Sutter's Volumetric Analysis, page 106 and also in Jour. Soc. Chem. Ind., 1898, p. 1106.

By Permanganate.

Weigh 0.5 gram of the sample into a platinum crucible and mix intimately, by stirring with a glass rod, with ½ gram of finely powdered dry solution carbonate. Brush off the rod into the crucible with a camel's-hair brush. Cover the crucible and place over a low flame. Gradually raise the temperature until the crucible is red hot. Then after a minute or two remove to the blast lamp and ignite for 5 minutes. Cool the crucible by plunging its bottom in cold water and place in a 400 cc. beaker. Cover with a watch glass and add 40 cc. of (1-4) hydrochloric acid (or 20 cc. of water and 20 cc. of hydrochloric acid, (1-1)). Heat on a hot plate until solution is complete. Lift out the crucible with a glass rod, bent in a crook at one end, and rinse it off into the beaker. Heat the contents of the beaker to boiling, add ammonia until alkaline, and then 10 cc. of a ten per cent. solution of oxalic acid, and proceed as directed on page 189.

This method will be found very useful in checking the acid and alkali determinations.

DETERMINATION OF SILICATES

·In order to better control the mixture of raw materials it is often of advantage to determine the insoluble matter or silicates. This practice differs considerably at different works, but the following will illustrate the general run of methods.

By Solution and Precipitation.

Weigh 0.5 gram of the sample into a porcelain dish or casserole, add 10 cc. of dilute (1-1) hydrochloric acid and a few drops of nitric acid, and evaporate to dryness, as rapidly as possible, without spattering. Bake at about 120° C. until all odor of acid has disappeared from the contents of the dish. Cool the latter, add 10 cc. of dilute (1-1) hydrochloric acid and cover with a watch glass. Heat for a few minutes and add 50 cc. of hot water. Boil a few minutes and add ammonia in faint excess. Boil a little longer, allow to settle and filter. Wash with hot water a few times, ignite and weigh. The residue is called "the silicates" and should, provided the mix is of proper composition, bear a certain ratio to the percentage of carbonate of lime. This ratio varies at different mills, but the figure is usually around 3.6.

By Solution.

Weigh 0.5 gram of the mixture into a beaker and boil with 10 per cent. hydrochloric acid for five minutes. Filter off the insoluble matter, wash, ignite and weigh. This method is in use in the laboratories of the Sandusky Portland Cement Co., and the mix is so proportioned as to give a certain ratio between this "insoluble matter" and the lime. This ratio varies at the two mills of the company. At the Sandusky mill the ratio is 3.9 and at the Syracuse mill it is 4.2, the higher ratio being due to the more silicious clay at the latter point.

COMPLETE ANALYSIS OF CEMENT MIXTURE OR SLURRY.

Method of the Committee on Uniformity in Analysis of Materials for the Portland Cement Industry of the New York Section of the Society of Chemical Industry.

One-half gram of the finely powdered substance is weighed out and strongly ignited for 15 minutes, or longer if the blast is not powerful enough to effect complete conversion to cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, and the analysis completed as directed on page 170, by moistening with water and digesting with hydrochloric acid, etc.

The above method is tedious and so cumbersome and long as to preclude its use in cement mill laboratories, where samples of the mix are analyzed daily, except for the preparation of standard samples. Even these should be analyzed also by the method in daily use in the laboratory in order to get all the work on the same relative basis and the longer and more accurate results should only be used to check the shorter mill scheme, and to make sure that the results of the latter are not too wide of the truth. The results which should actually be used as the values for the carbonate of lime, etc., in the samples should be those obtained by the regular mill scheme. If this is not done, acid and alkali will give one set of results and a complete analyses another, etc.

The scheme given below is modeled after those generally in use in cement mill laboratories and combines a fair degree of accuracy with rapidity and convenience of execution.

Method of the Committee on the Analysis of Portland Cement and Cement Materials of the Lehigh Valley Section of the American Chemical Society.

Weigh 0.5 gram of the finely ground sample into a small platinum crucible and mix intimately, by stirring with a glass rod, with 0.5 gram of pure dry finely powdered sodium carbonate. Brush off the rod into the crucible with a camel's-hair brush. Cover the crucible and place over a low flame. Gradually raise the latter, until the crucible is red hot, and continue heating, in the full flame of the Bunsen burner, for five minutes longer; then place over a blast lamp and heat for five minutes more. Cool and place the crucible on its side in a porcelain casserole or dish, or preferably a platinum dish, and dissolve the mass in 10 cc. of water and 10 cc. of hydrochloric acid. Heat until solution is complete, keeping the dish covered to avoid loss by effervescence. When everything, except a little gelatinous silica, which usually separates out, is in solution, remove the crucible and clean off into the dish with a rubber-tipped rod. Evaporate to dryness at a moderate heat, continuing to heat the mass—not above 200° C. —until all odor of acid is gone. Do not hurry this baking or skimp the time. The whole success of the analysis depends on thoroughness at this point. Cool; add 20 cc. hydrochloric acid (1-1); cover, and boil gently for ten minutes; add 30 cc. water, raise to boiling, and filter off the silica; wash with hot water four or five times; put in crucible, ignite (using blast for 10 minutes), and weigh as SiO_2.

Iron and Alumina.

Make filtrate alkaline with ammonia, taking care to add only slight excess; add a few drops of bromine water and boil till odor of ammonia is faint. Filter off the hydroxides of iron and aluminum, washing once on the filter. Dissolve the precipitate with hot dilute nitric acid, reprecipitate with ammonia; boil five minutes; filter and wash the iron and alumina with hot water once; place in crucible, ignite carefully, using blast for 5 minutes, and weigh combined iron and aluminum oxides.

Iron.

If it is desired to separate the two oxides add four grams acid potassium sulphate to the crucible and fuse at a very low heat until oxides are wholly dissolved—twenty minutes at least; cool; place crucible and cover in small beaker with 50 cc. water; add 15 cc. dilute sulphuric acid (1-4); cover and digest at nearly boiling until melt is dissolved; remove crucible and cover, rinsing them carefully. Cool the solution and add 10 grams powdered C. P. zinc, No. 20. Let stand one hour, decant the liquid into a larger beaker, washing the zinc twice by decantation, and titrate at once with permanganate. Calculate the Fe_2O_3 and determine the Al_2O_3 by difference. Test Zn, etc., by a blank and deduct.[1]

Lime.

Make the filtrate from the hydroxides alkaline with ammonia; boil; add 20 cc. boiling saturated solution ammonium oxalate; continue boiling for five minutes; let settle and filter. Wash the calcium oxalate thoroughly with hot water, using not more than 125 cc., and transfer it to the beaker in which it was precipitated, spreading the paper against the side and washing down the precipitate first with hot water and then with dilute sulphuric acid (1-4); remove paper; add 50 cc. water, 10 cc. Conc. sulphuric acid, heat to incipient boiling and titrate with permanganate, calculating the CaO.

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[1] Iron may also be determined by using a separate sample, igniting with half its weight sodium carbonate, dissolving the mass in hydrochloric acid and titrating with stannous chloride as directed on page 196, or the iron may be precipitated with ammonia redissolved in sulphuric acid, and the iron determined by reduction with zinc and titration with permanganate. (See page 190).

Magnesia.

If the filtrate from the calcium oxalate exceeds 250 cc.; acidify, evaporate to that volume; cool, and when cold add 15 cc. strong ammonia and with stirring 15 cc. stock solution of sodium hydrophosphate. Allow to stand in the cold six hours or preferably over night; filter; wash the magnesium phosphate with dilute ammonia (1-4) plus 100 gms. ammonium nitrate per liter; put in crucible, ignite at low heat and weigh the magnesium pyrophosphate.

OTHER CONSTITUENTS.

For the determination of sulphur, carbon dioxide, hygroscopic and combined water, and alkalies, refer to the methods given under cement. The fusion method is to be used for determining sulphur, which is usually present as sulphide (iron pyrites) or in combination with organic matter in mixtures of marl and clay. Calcium sulphate may be determined by simple solution in hydrochloric acid as in cement.

CHAPTER XI.

THE ANALYSIS OF THE RAW MATERIALS.

SAMPLING.

Limestone and Cement Rock.

Limestone deposits should be sampled by means of core or churn drills, sinking the test holes to a considerable depth. Surface samples, knocked off here and there, are of no value and the time spent in analyzing any number of them is, in most cases, thrown away. In sampling limestone or other solid material, the surface dirt and clay should be shoveled away and the weathered rock removed. The drill can then be set up and the sample taken. In prospecting a limestone property, it is usual to make a map showing the topography, etc., and this should be divided into squares having sides of say 50 to 300 feet. Drill holes can then be sunk at the corners of each square and the cores or chips brought up by the drill saved for analysis. Usually it is the custom, instead of making one sample of all the rock brought up by the drill from a hole, to make separate samples of the material brought up from various depths. Thus one sample would represent the material brought up from a depth of hole from 0 to 10 feet, while the next would represent that taken by the drill in going from 10 to 20 feet, etc. By doing this, the uniformity of the deposit, as well as its freedom from bands of magnesium stone, etc., can be tested.

After the analyses are all made, charts or plots should be drawn showing the amount of stripping to be done (dirt to be removed), the quality of the rock at various depths and, if the drilling is carried far enough, the depth of the deposit at each point. This can be shown easiest by means of sections, cutting the deposit, along the line of squares, drawn to scale and showing, by means of various kinds of shading, the stripping, etc. From these charts the amount of rock available and the earth which must be removed to get at this can be calculated. In many quarries the material removed by the drill, in preparing for a blast, is used as a sample in order to give the chemist the data for making the mixture of limestone and clay.

The churn drill is made by the Ingersoll-Rand Drill Co., the Keystone Driller Co., and others, and consists of a cylinder mounted on a heavy tripod and provided with a piston to which is attached the drill rod. The cutting edge of the latter is usually in the form of an X and each cutting edge is about 4 inches long. Either air or steam can be used to operate the drill, though the latter is almost always used in prospecting, as a small portable boiler is all that is needed to supply this. The drilling of test holes should always be in the hands of an experienced driller.

The chips or mud from the churn drill should be dried, if necessary, and sent to the laboratory in clean bags of cloth or paper, or in round tin boxes, etc. There the sample should be crushed and quartered down to laboratory dimensions—the final sample being made to pass a 200-mesh sieve.

Core drills are also much used in prospecting limestone. These cut a round cylinder or core of rock, 2 or 3 inches in diameter, as they pass into the rock. For some purposes these cores are very valuable, as they allow an inspection of the sample as to stratification, etc., and any thin bands of quartz, etc., are shown at once. The drills themselves are expensive, however, and troublesome to operate and repair, as the cutting is done by means of diamonds set in the end of the drill. Recently the Davis-Calyx Drill Co., has brought out a core drill which works on a different principle and which has given excellent satisfaction.

Clay and Shale.

Clay can be sampled in a number of ways, such as by digging pits or sinking test holes by means of an auger drill or a serrated pipe. Hard clays and shales will require either the auger or churn drill. The churn drill has been described in the preceding section, and the auger drill, for use in sampling, is similar to those used for coal cutting, etc. The serrated pipe consists of a pipe, the end of which has been filed and tempered to form sharp teeth like a saw. This is forced down into the clay by twisting a handle at the upper end. The result, when withdrawn, is a plug of clay, filling the pipe and representing the strata through which the latter has passed.

Clay deposits should be mapped out carefully, as different parts of the bed may show very different proportions of silica and alumina, and in order to get a cement with uniform setting properties it may be necessary to work two or more parts of the deposit in conjunction, in order to keep the ratio between the silica and alumina constant.

The depth of the deposit should also be determined so that a calculation of the available quantity of clay may be made.

Marl.

For sampling marl, a tube, similar to that used for sampling cement, may be employed to advantage. This is described on page 168, or the serrated pipe described before may be used. If the marl deposit is very wet, a long pipe having a plug at one end may be used.' This plug should be of iron, have a sharp point, fit the mouth of the pipe closely and be fastened to a long thin iron rod. In using the sampler, the iron plug is drawn up against the mouth of the pipe and the latter is thus shoved down to the depth at which the sample is to be taken. The pipe is then raised and shoved down to its former level, being forced tight against the iron plug. The pipe is then raised by means of the rod and the sample dumped out.

An excellent sampler can also be made from two pieces of brass pipe similar to the grain sampler described on page 169.

Marl deposits should be very thoroughly mapped out, not only as to quality, but also as to the depth of the deposit in order that the quantity available for manufacturing purposes may be calculated, since the value of marl deposits depends in most cases as much upon quantity as quality.

METHODS FOR LIMESTONE, CEMENT-ROCK AND MARL.

By Ignition of the Sample with Sodium Carbonate.

Silica.

Weigh 0.5 gram of finely ground dried sample into a platinum crucible and mix intimately with 0.5 gram of pure dry sodium carbonate by stirring with a glass rod. Place the crucible over a low flame and gradually raise this latter until the crucible is red hot. Continue heating for five minutes, then substitute a blast lamp for the Bunsen burner and heat for five minutes longer. Place the crucible in a dish or casserole, add 40 cc. of water and 10 cc. of hydrochloric acid, and digest until all the mass is dissolved out of the crucible. Clean off the crucible inside and outside, add a few drops of nitric acid to the solution and evaporate it to dryness. Heat the residue at 110° C. for one hour, cool, add 15 cc. of dilute hydrochloric acid, cover with a watch glass and digest for a few minutes on the hot plate. Dilute with 50 cc. of hot water, heat nearly to boiling, and filter. Wash the residue well with hot water. Dry, ignite, and weigh as silica, SiO_2.

If the limestone is high in silica a trace will be found in the filtrate from the silica as precipitated above. If great accuracy is desired, after evaporation to dryness, dissolve the mass in the dish in hydrochloric acid and water as usual without heating it to 110° C. for one hour and filter and wash. Evaporate the filtrate to dryness, and again dissolve in water and hydrochloric acid, filter, and wash. Ignite the two precipitates together and weigh as SiO_2.

Ferric Oxide and Alumina.

Heat the filtrate to boiling, add ammonia in slight but distinct excess, boil for five minutes and filter. Wash the precipitate twice with hot water. Remove the filtrate from under the funnel and in its place stand the beaker in which the precipitation was made. Dissolve the precipitate in dilute nitric acid and wash the filter-paper free from iron with cold water. Heat the solution to boiling and precipitate the iron and alumina with ammonia as before. Filter, allowing the filtrate to run into that from the first precipitation, wash once with hot water, dry and ignite. Weigh and report as ferric oxide and alumina.

If the percentage of ferric oxide and alumina are desired separately, proceed as directed in A, B, or C.

A. Fuse the precipitate of ferric oxide and alumina, after weighing, with a little sodium carbonate, dissolve in a little water to which a few cubic centimeters of hydrochloric acid have been added, and drop into the solution a few small crystals of citric acid. Add ammonia until the solution smells slightly of the reagent, and then an excess of ammonium sulphide. Allow the black precipitate to settle, filter, wash a few times, dissolve in hydrochloric acid, add a little bromine water, boil a while and add ammonia in slight but distinct excess. Filter, wash well with hot water, ignite and weigh as Fe_2O_3. Deduct this weight from that of the total ferric oxide and alumina, for the weight of alumina, Al_2O_3.

B. Fuse the precipitate of ferric oxide and alumina, after weighing, with caustic potash in a silver crucible or dish. Treat the fusion with water, boil, filter, and wash. Dry, ignite, and weigh the residue as ferric oxide, Fe_2O_3. Deduct this weight from that of the ferric oxide and alumina, for the weight of alumina, Al_2O_3.

C. Dissolve the residue, after fusion with sodium carbonate, in a little dilute hydrochloric acid and determine the ferric oxide volumetrically by the method given on page 196.

Lime.

Heat the filtrate from the iron and alumina, which should measure between 300 and 500 cc., to boiling and add 25 cc. of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and allow the precipitate one hour in which to settle. Filter and wash well with hot water. After washing, treat the precipitate as directed below in *A* or *B*.

A. Dry the precipitate by heating over a low flame, in a weighed platinum crucible, ignite until all carbonaceous matter is destroyed and ignite for fifteen minutes over a blast lamp. Cool and weigh. Again ignite for five minutes over a blast lamp and weigh. If this weight agrees to within 0.0002 gram of the former one it may be taken as the weight of the calcium oxide, CaO. If it does not agree, ignite again and repeat, if necessary, until the weight is constant.

B. Punch a hole in the filter paper and wash the precipitate into the beaker in which the precipitation was formed. Wash the paper with dilute sulphuric acid from a wash bottle and then with hot water. Dilute the solution to 300 or 40 cc., heat to 60° or

70° C., and after adding 10 cc. of dilute sulphuric acid titrate with permanganate. Calculate the per cent. of lime, CaO, or calcium carbonate, $CaCO_3$, in the limestone, as directed under "Volumetric Determination of Calcium," page 185.

Magnesia.

To the filtrate from the calcium oxalate add sufficient hydrochloric acid to make it slightly acid, and 30 cc. of sodium phosphate solution. Concentrate to about 300 cc. by evaporation. Set the solution in a vessel of cold water and when cooled to the temperature of the latter add ammonia, drop by drop, from a burette, with constant stirring until slightly ammoniacal and the precipitate begins to form. Stop adding ammonia and stir for five minutes, add one-tenth the volume of the liquid of strong ammonia and continue the stirring for three minutes more. Allow the solution to stand in a cool place over night, filter, wash well with a mixture of 1000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.36190 for its equivalent of magnesia, MgO, or by 0.75722 for magnesium carbonate, $MgCO_3$.

By Solution in Hydrochloric Acid.

Insoluble Silicious Matter.

Weigh 0.5 gram of the finely ground dried sample into a porcelain dish or casserole, cover with a watch glass and add 30 cc. of water and 10 cc. of concentrated hydrochloric acid. Warm until all effervescence has ceased, uncover, add a few drops of nitric acid, and evaporate to dryness. Bake on the hot plate or sand-bath until all odor of hydrochloric acid has disappeared, or safer still, heat in an air bath at 110° C. for one hour after the residue has become perfectly dry. Cool the dish and add 5 cc. of dilute hydrochloric acid, set on the hot plate, covered with a watch glass for five minutes, then add 50 cc. of hot water and filter, after digesting until all except silicious matter dissolves. Wash thoroughly, ignite and weigh as "insoluble silicious matter."

Silica.

Should it be desirous to know the silica in the "insoluble silicious matter" fuse it with ten times its weight of pure dry sodium carbonate, first over a Bunsen burner turned low, and then, after slowly raising the flame of this latter to its full height, over a blast lamp until the contents of the crucible are in a state of quiet fusion. Remove the crucible from the lamp and run the fused mass well up on its sides by tilting and revolving the crucible while held with the crucible tongs. While still hot dip the crucible three-quarters of the way up in a pan of cold water which will frequently cause the mass to loosen from the crucible. Wash off any material spattered on the crucible cover into a casserole or dish with hot water, and add the mass in the crucible if it has become detached. If not, fill the crucible with hot water and set on the hot plate until the fused mass softens and can be removed to the casserole. Dissolve any particles of the mass in hydrochloric acid, that adhere too firmly to the crucible to be removed by gentle rubbing with a rubber-tipped rod. When the hot water has thoroughly disintegrated the fused mass, cover the casserole or dish with a watch glass and strongly acidify the contents with hydrochloric acid. Heat until all effervescence ceases and everything dissolves except the silica. Wash off the watch glass into the dish and evaporate the solution to dryness. Heat for one hour at 110° C. in an air-bath, or on the hot plate at not too high a temperature until all odor of hydrochloric acid has disappeared from the dry mass. Cool, add 10 cc. of hydrochloric acid and 50 cc. of water, warm until all soluble salts are in solution, filter, wash well with hot water, dry, ignite, and weigh as silica, SiO_2.

$Fe_2O_3, Al_2O_3, CaO, MgO$.

Mix the two filtrates from the silica separations and proceed to determine iron and alumina, lime and magnesia, as directed in the method "By Ignition with Sodium Carbonate."

When the amount of sodium carbonate added to the "insoluble silicious matter" is greater than 0.5 gram, it is best in very accurate work, instead of mixing the two filtrates from the silica, to determine the iron, alumina, lime, and magnesia in each solution separately, since the large lime precipitate is almost sure to be contaminated with sodium salts if the two filtrates are mixed.

Determination of Organic Matter, Insoluble Silicious Matter, Ferric Oxide and Alumina, Lime and Magnesia.

Weigh 1 gram of the finely ground dried limestone into a porcelain dish or casserole; cover with a watch glass and add 30 cc. of water and 10 cc. of concentrated hydrochloric acid. Warm until all effervescence ceases, uncover and evaporate to dryness on a water bath. Heat the dish for one hour, after the residue becomes thoroughly dry, at 110° C. in an air-bath. Cool the dish and add 5 cc. of hydrochloric acid and 50 cc. of hot water. Heat until all soluble salts dissolve, filter upon a Gooch crucible or a small counterpoised filter paper. Wash well with hot water, dry at 100° C. in an air-bath and weigh as "organic matter" plus "insoluble silicious matter."

Now ignite until all carbonaceous matter is destroyed, and cool and weigh as "insoluble silicious matter." This weight subtracted from the preceding one gives the "organic matter." If the silica in the "insoluble silicious matter" is desired, fuse the latter with ten times its weight of sodium carbonate and proceed as described in the preceding scheme for the analysis of limestone "By Solution in Hydrochloric Acid."

Heat the filtrate from the "organic matter" and the "insoluble silicious matter" to boiling, add ammonia in slight but distinct excess, and proceed to determine the ferric oxide and alumina, lime and magnesia, as directed on page 255.

The Determination of Alkalies, Sulphuric Acid, Carbon Dioxide, Combined Water and Loss on Ignition.

For the determination of these constituents refer to the methods given under cement.

Rapid Determination of Lime and Magnesia.

S. B. Newberry[1] suggests the following rapid scheme for determining lime and magnesia in limestone, etc. "Prepare one-fifth normal hydrochloric acid and one-fifth normal caustic soda solutions, and standardize with pure, transparent Iceland spar. One-half gram of spar should exactly neutralize 50 cc. of acid.

Weigh out one-half gram of finely-ground limestone, transfer to an Erlenmeyer flask of about 500 cc. capacity, provided with

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[1] Cement and Engineering News, March, 1903, p. 35.

rubber stopper and thin glass tube about 30 inches long to serve as a condenser, as described on page 236. Run into the flask 60 cc. one-fifth normal acid; attach the condenser and boil gently, allowing no steam to escape from the tube, for about two minutes. Wash down the tube into the flask with a few cc. of water from wash-bottle; remove the condenser and *cool the solution thoroughly* by immersing the bottom of the flask in cold water. When quite cold, add five drops of phenolphthalein solution, (1 gm. in 200 cc. alcohol), and titrate back to first pink color with one-fifth normal soda solution. It is important to recognize the point at which a faint pink color first appears throughout the solution, even though this may fade out in a few seconds. If alkali be added to a permanent and strong red color, the lime will come too low. Let us call the amount of acid used the *first acid,* and the alkali used to titrate back the *first alkali.*

"Transfer the neutral solution to a large test tube, twelve inches long and one inch inside diameter, marked (with a paper strip or otherwise) at 100 cc. Heat to boiling, and add one-fifth normal soda solution, about one cc. at a time, boiling for a moment after each addition, till a deep red color, which does not become paler on boiling, is obtained. This point can be easily recognized within one-half cc. after a little practice. Note the no. of cc. soda solution added to the neutral solution, as *second alkali.* Dilute to 100 cc., boil for a moment, and set the tube aside to allow the precipitate to settle. When settled, take out 50 cc. of the clear solution by means of a pipette, and titrate back to colorless with one-fifth normal acid. Multiply by 2 the no. of cc. acid required to neutralize, and note as *second acid.*

"The calculation is as follows:

Second alkali — second acid, $\times 2 \times 0.40 = \%$ MgO.

First acid — (first alkali + second alkali — second acid), $\times 2 \times 0.56 = \%$ CaO.

"Example: To one-half gram limestone were added 60.00 cc. acid, (*first acid*). To titrate back to first pink, 11.60 cc. alkali were required, (*first alkali*). The solution was then transferred to test tube, boiled, and 3.55 cc. alkali added to permanent deep red color, (*second alkali*). After diluting to 100 cc. and settling, 50 cc. of the red solution required 0.45 cc. acid to decolorize it, ($0.45 \times 2 = 0.90 =$ *second acid*).

$3.55 - 0.90, \times 2 \times 0.40 = 2.12\%$ MgO.

$60.00 - (11.60 + 3.55 - 0.90) \times 2 \times 0.56 = 51.24\%$ CaO.

NOTES.

"Nitric acid may be used in place of hydrochloric; the latter appears, however, to give slightly better results.

"Not more than 1 c.c. excess of alkali should be added in precipating the magnesia; the "second" should therefore not exceed 1.0. Larger excess of alkali tends to throw down lime.

"The settling usually requires only a few minutes, unless much magnesia is present; it may be greatly hastenend by allowing the test-tube to stand two or three minutes, then immersing the lower part for a moment in cold water..

" If results are desired in persentages of magnesium carbonate and calcium carbonate, the factors 0.84 and 1.00 are to be substituted for 0.40 and 0.56, respectively.

"The tendency of the method is to give slightly too high results on magnesia and too low results on lime. This is partly due to the formation of calcium carbonate, by the action of the carbon dioxide of the air, during the precipitation of the magnesia. By the use of a large test-tube, as above described, this error is so far reduced as to be insignificant. Another source of shortage of lime is to be found in the presence, in certain materials, of small proportions of lime in a form insoluble in dilute acid."

In determining lime in cement rock or in cement mixtures made from clay containing calcium silicates this method always gives low results for the above reason. To use the method on such material it is necessary to determine a "correction factor" by comparison between the lime found by this method and that on page 189, in a series of standard samples. By subtracting the lower from the higher results, a constant is obtained which is to be added to all results obtained by titration with the acid and alkali.

METHODS FOR CLAY.

Silica.

Finely grind the sample of clay and heat at 100° to 110° C. for one hour in an air-bath. Transfer 1 gram of the dried clay to a fairly large platinum crucible. Mix with it by stirring with a smooth glass rod 10 grams of sodium carbonate and a little sodium nitrate. Heat over a Bunsen burner, gently at first, for a few minutes and then to quiet fusion over a blast lamp. Run the fused mass well up on the sides of the crucible and allow to cool. Nearly fill the crucible with hot water and set on the hot plate for a few minutes. Pour the solution and as much of the mass as has become detached from the crucible into a casserole or better a platinum dish. Repeat this treatment until the mass has become thoroughly disintegrated. Treat what remains in the crucible with dilute hydrochloric acid and pour the acid into the casserole or dish. Clean out the crucible with a rubber-tipped rod and after acidifying with hydrochloric acid evaporate the contents of the casserole to dryness. Proceed as in *A* or *B*.

A. Heat in an air-bath at 110° C. for one hour, or until all odor of hydrochloric acid has vanished. Cool, moisten the mass with dilute hydrochloric acid, add a little water and again evaporate to dryness. Now add 30 cc. of dilute hydrochloric acid, digest at a gentle heat for a few moments and add 100 to 150 cc. of hot water. Allow to stand a few minutes on the hot plate and filter. Wash the residue thoroughly with hot water, ignite over a Bunsen burner until all carbon is burned off, and then for five minutes over a blast lamp, and weigh as SiO_2.

B. The residue, without further heating, is treated at first with 10 cc. of dilute HCl. The dish is then covered and digestion allowed to go on for 10 minutes on the bath, after which the solution is diluted slightly, filtered, and the separated silica washed thoroughly with hot water. The filtrate is again evaporated to dryness, the residue, without further heating, taken up with acid and water, and the small amount of silica it contains separated on another filter paper. The two papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for 15 minutes. The precipitate is then weighed as SiO_2. This precipitate is more or less contaminated by iron oxide and alumina. In accurate work the amount of these must be determined in the following manner and deducted from the weight of SiO_2 as found above. Moisten the weighed silica with a few drops of dilute sulphuric acid and half fill the crucible with hydrofluoric acid. Evaporate to dryness by placing over a burner in an inclined position so that the low flame plays upon the side of the crucible and the evaporation takes place only from the surface. Ignite and weigh. The difference between the two weights is the silica, SiO_2.

Ferric Oxide and Alumina.

Add a few drops of bromine water and heat the filtrate from the silica, which should measure about 150 cc., to boiling, and add ammonia in slight but distinct excess; boil for a few moments and allow the precipitate to settle. Filter and wash several times with hot water. Remove the filtrate from under the funnel and dissolve the precipitate of iron and alumina in a mixture of 15 cc. of dilute nitric acid and 15 cc. of cold water, by pouring back and forth through the filter as long as any precipitate remains. Wash the filter paper well with cold water, dry, place in the weighed platinum crucible containing the residue from the purification of the silica if this has been done, and set aside. Reprecipitate the iron and alumina in the filtrate as before by adding a slight but distinct excess of ammonia, filter, and wash once with hot water. Place in the crucible with the other paper and ignite, using the blast as in determining silica and weigh as

$$Fe_2O_3 + Al_2O_3(TiO_2 + P_2O_5 + Mn_3O_4).$$

Determine the ferric oxide in the precipitate as in *A, B* or *C* below and subtract the amount from this weight; the difference will be the $Al_2O_3(TiO_2 + P_2O_5 + Mn_3O_4)$.

A. Fuse the ignited precipitate with sodium carbonate, treat the fused mass with hot water and wash it out into a small beaker, allow the residue to settle and decant off the clear supernatant liquid through a small filter, leaving the residue in the bottom of the beaker. Wash the filter paper once and pour a little hot concentrated hydrochloric acid through the filter into the beaker containing the residue. Heat gently, but do not boil. When all the residue is dissolved, determine the iron in the solution by reduction with stannic chloride and titration with potassium bichromate as directed on page 196.

B. The precipitate is fused with 3 or 4 grams of potassium bisulphate at a very low temperature and the melt is dissolved in water acidified with sulphuric acid. The solution is then reduced with zinc or hydrogen sulphide, (preferably the latter since clays sometimes contain considerable titanic oxide), and the iron determined as directed on page 190.

C. Brush the ignited precipitate into a small beaker, cover with a mixture of 6 cc. of water and 16 cc. of concentrated sulphuric acid, and covering with a watch glass, digest on a hot plate or sand-bath until all dissolves, except possibly a residue of silica. Filter, if necessary, and determine the iron by reduction with zinc and titration with standard permanganate as directed on page 171.

Lime.

Heat the filtrate from the iron and alumina to boiling and add an excess of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and set aside for several hours to allow the complete precipitation of the lime. Filter, wash, dry, and ignite over a blast lamp until the weight is constant. Weigh as calcium oxide, CaO.

Magnesia.

To the filtrate from the calcium oxalate add sufficient hydrochloric acid to make it slightly acid and then 30 cc. of sodium phosphate solution. Concentrate the solution to about 300 cc. by evaporation and cool. Then add ammonia drop by drop, with constant stirring until the liquid is slightly ammoniacal and the precipitate begins to form. Stop adding ammonia and stir for five minutes, then add one-tenth the volume of the liquid of strong ammonia and continue the stirring for five minutes more. Allow the solution to stand in a cool place over night, filter, wash with a mixture of 1000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite (do not use the blast lamp), and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.36190 for magnesium oxide, MgO.

Notes.

Clay is practically unacted upon by hydrochloric acid and requires fusion with alkaline carbonates for its decomposition.

Should the solution, on evaporation to dryness, show a tendency to climb the sides of the dish, greasing the latter lightly with vaseline or paraffin will remove the difficulty.

The amounts of lime and magnesia in clays are small, so that the filtrate and washings from the second ammonia precipitation of the iron and alumina may be rejected and the lime and magnesia determined in the first filtrate only. For the same reason it is unnecessary to reprecipitate the calcium oxalate, although the solution is largely contaminated by sodium salts from the alkaline fusion.

Determination of Free, Hydrated and Combined Silica.[1]

To ascertain how much of the silica found exists in combination with the bases of the clay, how much as hydrated acid, and how much as quartz sand or as a silicate present in the form of sand, proceed as follows:[2]

Let A represent silica in combination with the bases of the clay.

Let B represent hydrated silicic acid.

Let C represent quartz sand and silicates in the form of sand, *e. g.,* feldspar sand.

Dry 2 grams of the clay at a temperature of 100° C., heat with sulphuric acid, to which a little water has been added, for eight or ten hours, evaporate to dryness, cool, add water, filter out the undissolved residue, wash, dry, and weigh $(A + B + C)$. Then treat it with sodium carbonate. Transfer it, in small portions at a time, to a boiling solution of sodium carbonate contained in a platinum dish, boil for some time and filter off each time, still very hot. When all is transferred to the dish, boil repeatedly with strong solution of sodium carbonate until a few drops of the liquid finally passed through the filter remain clear on warming with ammonium chloride. Wash the residue, first with hot water, then (to insure the removal of every trace of sodium carbonate which may still adhere to it) with water slightly acidified with hydrochloric acid, and finally with water. This will dissolve $(A + B)$ and leave a residue (C) of sand, which dry, ignite, and weigh.

To determine (B), boil 4 or 5 grams of clay (previously dried

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[1] Cairns' *Quantitative Chemical Analysis*, page 68.

[2] Compare Fresenius' *Quantitative Analysis*, 5th Ed., 1865, sec. 236.

at 100° C.) directly with a strong solution of sodium carbonate in a platinum dish as above, filter and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and determine the silica as usual. It represents (B) or the hydrated silicic acid.

Add together the weights of (B) and (C), thus found, and subtract the sum from the weight of the first residue (A+B+C). The difference will be the weight of (A) or the silica in combination with the bases of the clay.

If the weight of (A + B + C) found here to be the same as that of the silica found by fusion in a similar quantity in the analysis of the clay, the sand is quartz, but if the weight of (A + B + C) be greater, then the sand contains silicates.

The weight of the bases combined with silica to form silicates can be found by subtracting the weight of total silica found in 1 gram in the regular analysis, from the weight of (A + B + C) in 1 gram.

Notes.

The following scheme is much less trouble than that described above and gives the silica present as sand and silicates undecomposable by sulphuric acid and that in combination with the alumina or combined silica.

Heat 1.25 grams of the *finely* ground and dried (at 100° C.) clay with 15 cc. of concentrated sulphuric acid to near the boiling-point of the acid and digest for from ten to twelve hours at this temperature. *Cool,* dilute and filter. Wash and ignite the residue to a constant weight. Call this weight A. After weighing brush the residue which consists of silica present as sand and undecomposable silicates and silica from the decomposition of the silicates of alumina, into an agate mortar, grind very finely and weigh 0.5 gram of it into a platinum dish containing 50 cc. of *boiling* caustic potash solution (of 1.125 sp. gr.). Boil for five minutes, filter, wash, first with hot water and then with water containing a little dilute hydrochloric acid and then again with hot water, dry and ignite to a constant weight. Call this weight B. Multiply A by 0.4 (to correct the 1.25 grams of clay used to correspond to the 0.5 gram of the residue taken for treatment with caustic potash solution) and subtract B from the product. Multiply the difference by 200 for the per cent. of silica combined with alumina in the clay. This deducted from the total silica found by analysis gives the silica as sand and undecomposable silicates.

Determination of Coarse Sand.

In examining clay to be used for cement manufacture, it is not so important to know the chemical condition in which the silica exists as its physical state, *i. e.*, whether the sand grains are large or small. Pure quartz sand if sufficiently finely powdered will combine with lime at the temperature of the rotary kiln, so that what is most requisite in clay to be used for cement manufacture is that the sand shall be present in fine grains. To test the clay, along this line, weigh 100 grams of clay into a beaker and wet with water. Triturate to a thin slip with a glass rod and wash into a No. 100 test sieve. Now place the sieve under the tap and wash as much of the clay as possible through the meshes of the sieve with a gentle stream of water. Dry the sieve on a hot plate and brush out the dry residue failing to pass through it on to the balance pan and weigh. The weight in grams gives the percentage of the clay failing to pass a No. 100 sieve. The clay may also be tested in a similar manner on the No. 200 sieve and the residues may be subjected to chemical analysis.

Marls are examnied by the same method to determine fineness.

Determination of Water of Combination.

Should the clay contain very little organic mater, iron pyrites or calcium carbonate, heat 1 gram of the previously dried cement for twenty minutes to a bright redness over a Bunsen burner. The loss in weight will represent the water of combination. If, however, the clay contains much organic matter, calcium carbonate or iron pyrites, the water of combination should be determined by absorption in a weighed calcium chloride tube as described for cement analysis on page 208.

Many chemists simply heat 1 gram of dried clay over a blast for twenty minutes reporting the loss of weight as *loss on ignition*. This loss, of course, comes from combined water and carbon dioxide driven off (from the decomposition of carbonates), organic matter burned and iron pyrites changed from iron sulphide, FeS_2, to ferric oxide.

Sulphur and Iron Pyrites.

For the determination of sulphur in clay, proceed as directed for determining this constituent in cements by fusion with sodium carbonate and potassium nitrate. Multiply the weight of barium sulphate by 0.25845 and report as iron pyrites, FeS_2, or by 0.13734 and report as sulphur.

RAPID DETERMINATION OF SILICA, IRON OXIDE AND ALUMINA AND LIME.

Weigh 0.5 gram of the finely ground sample of clay into a platinum crucible and mix with it intimately, by stirring with a glass rod rounded at the ends, one gram of precipitated calcium carbonate such as is used for alkali determinations and one-half gram of finely powdered dry sodium carbonate. The mixing must be thorough. Brush off the rod into the crucible with a camel's hair brush and place the covered crucible over a Bunsen burner turned low. Gradually raise the flame till the full heat is attained, keep at this temperature for 2 or 3 minutes, and then remove to the blast lamp and ignite strongly for 5 minutes. Cool the crucible by plunging its bottom in cold water and place it on its side in a platinum or porcelain dish or casserole. Add 10 cc. of water and 10 cc. of dilute (1-1) acid. As soon as the mass is dissolved out of the crucible remove the latter, rinse it off into the dish removing any solid particles with a policeman and evaporate the solution to dryness. Heat the dish at 120° C. until all odor of acid has disappeared. Cool, add 20 cc. of hydrochloric acid (1-1), cover and boil a few minutes, add 50 cc. of water, boil a few minutes longer, filter, wash and ignite, first over the burner, until carbon is all burned off, and then over the blast for 10 minutes. Cool and weigh as silica, SiO_2.

Iron Oxide and Alumina.

Heat the filtrate to boiling, after adding a few drops of bromine water, add ammonia in slight but distinct excess and again heat to boiling. Continue boiling for two or three minutes and after allowing the precipitate to settle, filter and wash once with hot water. Invert the funnel over the beaker in which the precipitation was made and wash the precipitate back into this with a stream of hot water from a wash-bottle. Dissolve in dilute nitric acid, heat to boiling and reprecipitate with ammonia. Boil for a few minutes, allow the precipitate to settle, and filter. Wash once with hot water, ignite (using the blast finally) and weigh as oxides of alumina and iron, $Al_2O_3 + Fe_2O_3$.

Lime.

Weigh another sample of one gram into a platinum dish or a large crucible and add 10 cc. of dilute sulphuric acid (1-1) and approximately 5 cc. of hydrofluoric acid. Heat until fumes of sulphuric acid come off copiously. Cool and wash the contents of the dish into a 250 cc. beaker. Heat to boiling and add ammonia in slight but distinct excess. Redissolve the precipitate in 10 cc. of a 10 per cent. solution of oxalic acid, and dilute to 200 cc. Precipitate the lime with calcium oxalate as usual and determine as directed on page 189.

METHODS FOR GYPSUM OR PLASTER OF PARIS.

Determination of Silica, Iron Oxide, Alumina, Lime and Magnesia.

Weigh 0.5 gram of the finely ground sample into a platinum dish or porcelain casserole and add 20 cc. of dilute hydrochloric acid (1-1). Evaporate to dryness and heat the residue, at 110° C. until all odor of hydrochloric acid has vanished from the contents of the dish. Cool and add 10 cc. of dilute hydrochloric acid, cover with a watch glass and heat for 5 minutes. Dilute to 50 cc. and heat a little longer. Filter, wash the precipitate well with hot water, ignite and weigh. Report as insoluble silicious matter or proceed as follows: Instead of igniting and weighing fuse this insoluble residue after burning away the filter paper over a Bunsen burner with four or five times its weight of sodium carbonate (usually from 0.2-0.5 gram of the carbonate is enough), run the fused mass well up on the sides of the crucible and cool the latter suddenly by dipping its bottom in cold water. Place the crucible in a dish or beaker and dissolve out the fusion in a little dilute hydrochloric acid. Evaporate the solution to dryness and heat, at 110° C., until all odor of hydrochloric acid has disappeared from the dry mass. Dissolve in a little hydrochloric acid and water, as before, filter, wash, ignite and weigh as SiO_2.

Mix the above filtrate from the SiO_2 with that from the "insoluble silicious matter," heat to boiling, precipitate the iron and aluminum as oxides with ammonia and proceed as in the analysis of cements on page 173.

Determination of Sulphuric Acid.

Weigh 0.25 gram of the finely ground sample into a beaker and dissolve in 5 cc. of dilute (1-1) hydrochloric acid, by the aid of heat. Dilute to 100 cc. with hot water. Digest for a few minutes and filter. Wash the paper and residue thoroughly, with hot water, until the filtrate measures about 250 cc. Heat this latter to boiling and add, with constant stirring, 20 cc. of barium chloride solution, also boiling hot, and stir for five minutes. Remove from the source of heat and allow to stand over night in a warm place. In the morning, filter through a double filter paper or a "Shimer filter tube"[1] and wash well with hot water. Ignite (without using the blast) and weigh as $BaSO_4$. This weight multiplied by 0.34291 gives the SO_3 in the sample or by 0.62184 the $(CaSO_4)_2\,H_2O$ or by 0.7375 the $CaSO_4 . 2H_2O$. Do not forget a quarter gram sample has been taken.

Determination of Water.

Weigh one gram of the finely ground sample in a weighed platinum crucible and heat[2] for one hour at 100-105° C. Cool and weigh. The loss in weight represents the "moisture" or "water below 105° C."

Place the crucible over a Bunsen burner and heat at a *low* red temperature for thirty minutes. The loss in weight represents "water of combination" or "water above 105° C." If the heating has been too high, some sulphuric acid will have also been lost. To check this, dissolve the sample out of the crucible, after ignition, with hydrochloric acid. Dilute to about 100 cc. and filter into a 200 cc. flask. Wash well with hot water and dilute with water to the mark. Measure of this volume 50 cc. dilute to 250 cc. and determine the SO_3 as directed previously. If loss has occurred, this determination will give a lower figure than the other. In this case deduct the difference between the percentages found by

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[1] See page 206

[2] See page 218.

the two trials from percentage of loss in weight over the burner for the percentage of water of combination. If the heating of the crucible over the Bunsen burner has been done at a heat not higher than cherry red there should be no loss of sulphuric acid, however.

Determination of Carbon Dioxide.

Determine carbon dioxide as directed on page 215, for cement, using the evolution method.

PHYSICAL TESTING.

CHAPTER XII.

THE INSPECTION OF CEMENT.

Tests to be Made.

The qualities which are requisite for a good Portland cement are those which insure that concrete made from it shall be of sufficient strength to withstand any and all strains, stresses and shocks to which it may be submitted, not only when first made and allowed to harden, but after the lapse of many years. The tests now applied to cement all aim to search out these qualities, or show their absence, and may be classed under two general heads, i. e., those designed to show the strength of concrete made from the cement, and those designed to show its endurance. Under the first head come the tests for tensile strength, compressive strength, fineness to which the cement is ground, as this influences its sand-carrying capacity and hence its strength, and time or rate of setting, as quick-setting cement may not give sufficient time for proper manipulation of the concrete and slow-setting cement may take too long to get its strength. Under tests for endurance come the various so-called soundness tests, and possibly chemical analysis as the quantities of magnesia and of sulphur trioxide present are supposed to have an influence upon endurance.

Ordinarily cement is tested as to its:

(1) Soundness.
(2) Time of setting.
(3) Tensile strength alone (neat).
(4) Tensile strength with sand.
(5) Fineness to which it has been ground.
(6) Specific gravity.

Other tests are those of compressive and transverse strength, adhesion, abrasion, etc.

Method of Inspection.

It is now the custom to test carefully all cement to be used upon important work. Most of the large cities of the country maintain well equipped laboratories and systematically inspect all cement used upon the various municipal works undertaken by them. The various branches of the government, such as the War, Navy and Treasury Departments, each have one or more laboratories where the cement to be used in fortifications, dry-docks, public buildings, etc., is carefully tested. Various private laboratories also make a specialty of inspecting the cement to be used in big buildings, reservoirs, retaining walls, etc.,for private corporations, while the railroads, most of them, have well equipped laboratories for testing such materials, cement among them, as they purchase. Cement may be inspected either at the mill before shipment, or at the place where it is to be used, after receipt. The actual tests of course, may be made at either of these points, or the samples can be properly labelled and sent some distance to a convenient laboratory. The New York Rapid Transit Railroad (Subway) Commission pursued the former of these two plans and inspected the cement at the mill itself. The Philadelphia Rapid Transit Company, on the other hand, followed the latter plan and inspected the cement as received in Philadelphia. Both plans can be made to give entire satisfaction.

Where the product of one mill alone is to be used for the work the testing laboratory may be located at the mill from which the cement is supplied. Otherwise, it should, of course, be located at some convenient point to which samples can readily be sent.

The suggestion has been made to have the cement companies furnish the inspector testing appliances, quarters, etc., for doing this work. This seems to be asking rather much of the manufacturers, as their laboratories are, most of them, already overcrowded and the presence of an outsider, in the one part of the plant where trade secrets are likely to be exposed, is not desirable.

Inspection at the Mill.

Where cement inspection is done at the mill, certain bins are set aside by the proper authority at the cement mill, and the spouts leading into these are closed by means of a wire and lead seal such as is used in closing box cars; the idea of sealing the spouts is to prevent the bins from being emptied and refilled without the knowledge of the inspector. Any method which will insure against this, such as sealing wax and string will answer as well as the lead seal and wire. In some cases, it may be sufficient to rely upon the honesty of the mill authorities and to merely accept their word or promise that the bin has not been tampered with. Or an affidavit may be secured from the stock-house foreman to this effect.

After selecting the bin and insuring against its being emptied and refilled, it must be carefully sampled. How this is to be done will depend somewhat upon the size and shape of the bin. Since cement when freshly ground and hot flows not unlike a liquid, the the cement first run into the bin will be almost all of it deposited in a layer on the floor of the bin. For this reason, the means used for sampling the bin must be such that the cement at the bottom of the bin is included in the sample. On page 167, a rod such as is used by the inspectors of the Baltimore & Ohio Railroad is described. This is probably as satisfactory as any sampling device can well be. The taking of a sample from the floor of a bin may necessitate the use of a sledge hammer to drive the rod through the mass of cement in the bin. If the inspector is permanently located at the mill, the sample can be taken easiest, when the bin is filled, by means of an automatic sampler such as is described on page 226.

The importance of sampling the floor of a bin will be understood, when it is known that, in a bin of unsound cement, a sample taken only a few days after the bin has been filled and representing only the surface layer of cement will often be sound, while one representing the bottom layer may be unsound after even a month's seasoning.

The bin should be sampled in at least four places—the four corners—and may be sampled in as many more as the inspector sees fit. A sample drawn from the four corners of rectangular shaped bins, filled by a spout in the middle, will be representative. The feet and legs of the man taking the sample may be protected as he walks over the surface of the cement by thrusting them in clean, new cloth cement bags (a few of which can be found around all mills) and tying them securely around the legs above the knee. The cement sample should be placed in clean cloth bags, which should be properly closed and sealed and expressed or conveyed to the testing laboratory. If the inspecting laboratory is located at the mill, paper bags or tin buckets may be used for this purpose.

The objection has been raised to the use of cloth bags, that an unsound cement would probably be seasoned sound after a two or three days journey in them and some inspectors use tin buckets or cans, with tightly fitting covers, for this purpose. On the other hand, if an unsound sample is made sound by exposure in cloth bags after a few days journey by express, the inspector may rest assured that the body of the bin will be seasoned equally well by an equally long journey by freight in a box car. Also cement often leaves the mill "slow setting" and arrives at the work "quick setting," so that shipment of a sample in cloth should give a line on the likelihood of the main body of the cement doing this.

When the sample arrives at the testing laboratory, its receipt is properly recorded and the brand, manufacturer, bin, date sampled, etc., properly recorded, after which, to readily identify briquettes, etc., it is given a running number. The sample is then carefully mixed, and a sufficient quantity of this for the necessary tests is taken and passed through a 20-mesh sieve to remove lumps, after which it is submitted to the tests called for by the specifications. The large sample is then stored away for future reference, retests, etc.

When the results of the tests are at hand, the laboratory notifies its agent at the mill, who in turn informs the authorities of the cement company that such and such a bin is ready for shipment, and when cement is needed it is also the duty of the inspector to see that the cement is packed from accepted bins and accepted bins only.

This system usually necessitates the holding of a bin for from five to six weeks, if the specifications call for a 28 day test, or about two weeks if only the 7 day test is relied upon. This often puts the manufacturer to much inconvenience and trouble, but, from the standpoint of the consumer, seems to be preferable, since the manufacturer pays for the storage while the cement is being tested. On the other hand the manufacturer has the satisfaction of knowing that, after the cement is once shipped, it is off his hands for good and all with no chance for complaint from the purchaser.

Inspection on the Work.

When the cement is inspected as it arrives at the work, the cars are unloaded and sampled—one bag out of every 40 (or one barrel in ten) being selected and a sample drawn from it as indicated on page 166. These samples may be either mixed or kept separate in clean paper bags. The contents of each car should be piled in such a way that it may be kept to itself and marked by a properly tagged board or sign. When the work permits the use of a large store house, this should be divided into bins holding a carload, 150 barrels or 600 bags. The cement should be held in storage until the result of the tests are known when, if these are satisfactory, the contractor or foreman may be notified that he can use the cement from such and such a pile or bin.

When a car of cement fails to pass the specifications, the manufacturer is usually notified at once that such cement has been found unsatisfactory. He will then probably ask for a re-test, which should be made from new samples, drawn in the presence of his representatives, and, if possible, the tests also should be repeated in the presence of this representative. If this latter can not be done, the sample should be divided into three parts and placed in tin cans or fruit jars and closed up tight. One of these samples should be tested by the manufacturer and, unless his results agree with those of the consumer, the third sample should be sent to some reliable, competent third party with the agreement of both parties to stand by his results.

Should the cement finally be found unsatisfactory, it is usually returned to the manufacturer, who replaces it with another consignment or else a rebate is given upon it and it is used on some unimportant part of the job. Unsound cement may be held until it has been seasoned sound and quick setting cement may often be made slow setting by a small addition (0.5 per cent) of plaster or slaked lime. In both instances, the resulting concrete will be satisfactory and the manufacturer will usually be willing to bear the expense of storage, or addition of plaster or lime, rather than pay the double freight rate, necessary to its replacement with other cement. When the cement supplied by a manufacturer habitually fails to pass the specifications under which it is sold, he deserves little consideration from the engineer or inspector, but, when the failure of a brand to meet specifications is a rare incident, the engineer can afford to be lenient, if his work is not endangered thereby, especially if the average quality of the cement is far above that asked for by him, in his specifications.

Uniform Specifications and Methods of Testing.

In order to bring about uniformity both in the matter of inspection and of the specifications under which cement is sold, committees have been appointed by various scientific societies, chief of which have been the American Society for Testing Materials and the American Society of Civil Engineers. The latter society appointed a committee, some twenty years ago, to consider methods of testing cement and received its report in 1885. Later, another committee was appointed, which reported January 21st, 1903. This report was amended January 20th, 1904, and the methods of test recommended by it are now considered the standard ones.

The American Society for Testing Materials turned its attention to the drafting of a uniform set of specifications for cement, and its committee reported, June 17th, 1904. This set of specifications was endorsed by The American Institute of Architects, The American Railway Engineering and Maintenance of Way Association, The Association of American Portland Cement Manufacturers, and The American Society of Civil Engineers, and hence may be considered the "Standard Specifications."

In the following sections under the heading *"Specification"* are given the requirements as defined by the above set of specifications while under the heading, *"Method of Operating the Test,"* is given the method of testing recommended by the committee of the American Society of Civil Engineers in their report.

CHAPTER XIII.

SPECIFIC GRAVITY.

STANDARD SPECIFICATIONS AND METHOD OF TEST

Specification.—The specific gravity of the cement, thoroughly dried at 100° C., shall be not less than 3.10.

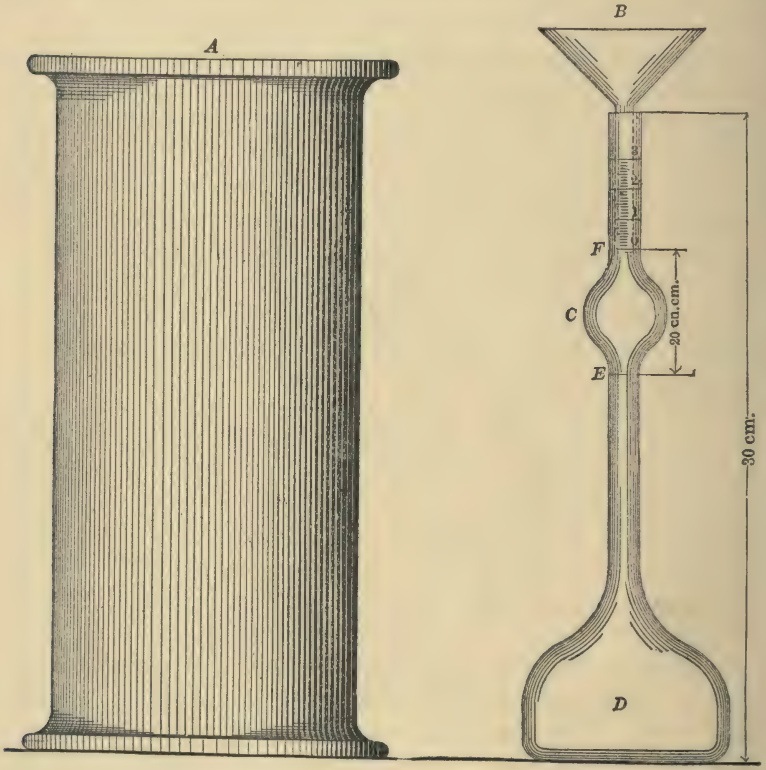

Fig. 65, Le Chatelier's Specific Gravity Apparatus.

Method of Operating the Test.—The determination of specific gravity is most conveniently made with Le Chatelier's apparatus. This consists of a flask *(D)*, Fig. 65, of 120 cu. cm. (7.32 cu. ins.)

capacity, the neck of which is about 20 cm. (7.87 ins.) long; in the middle of this neck is a bulb *(C)*, above and below which are two marks *(F)* and *(E)*; the volume between these marks is 20 cu. cm. (1.22 cu. ins.). The neck has a diameter of about 9 mm. (0.35 in.), and is graduated into tenths of cubic centimeters above the mark *(F)*.

Benzine (62° Baumé naphtha) or kerosene free from water, should be used in making the determination.

The specific gravity can be determined in two ways:

(1) The flask is filled with either of these liquids to the lower mark *(E)*, and 64 gr. (2.25 oz.) of powder, previously dried at 100° C. (212° F.) and cooled to the temperature of the liquid, is gradually introduced through the funnel *(B)* [the stem of which extends into the flask to the top of the bulb *(C)*], until the upper mark *(F)* is reached. The difference in weight between the cement remaining and the original quantity (64 gr.) is the weight which has displaced 20 cu. cm.

(2) The whole quantity of the powder is introduced, and the level of the liquid rises to some division of the graduated neck. This reading plus 20 cu. cm. is the volume displaced by 64 gr. of the powder.

The specific gravity is then obtained from the formula:

$$\text{Specific Gravity} = \frac{\text{Weight of Cement}}{\text{Displaced Volume}}$$

The flask, during the operation, is kept immersed in water in a jar *(A)*, in order to avoid variations in the temperature of the liquid. The results should agree within 0.01.

A convenient method for cleaning the apparatus is as follows: The flask is inverted over a large vessel, preferably a glass jar, and shaken vertically until the liquid starts to flow freely; it is then held still in a vertical position until empty; the remaining traces of cement can be removed in a similar manner by pouring into the flask a small quantity of clean liquid and repeating the operation.

OTHER METHODS.

With the Schumann-Candlot Apparatus.

Another form of apparatus in frequent use, particularly abroad, for taking the specific gravity of cement is that of Schumann as modified by Candlot. This apparatus (Fig. 66) consists of a graduated tube, B, terminated by a bulb, A. This tube fits tightly on the flask, D, by means of a ground joint. To use the apparatus, paraffin, turpentine, or benzine is introduced into the detached and inverted tube, B, in sufficient quantity to bring the level of the liquid above the zero point on the tube when the latter is in posi-

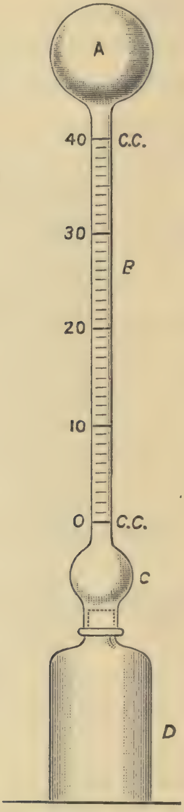

Fig. 66, Schumann Candlot Apparatus for Specific Gravity.

tion on the flask, D. A note is then made of this point, the tube is inverted and the flask detached. Into the latter is then introduced a known weight (usually 100 grams) of cement, and the flask is again connected with the tube. The whole apparatus is now agitated to expel air bubbles, then set in an upright position and the new height to which the liquid rises is read. The difference between this height and the last is the volume of liquid displaced by the cement. To find the specific gravity of the cement divide the weight of cement taken by the volume displaced, the result will be the specific gravity.

Jackson's Apparatus.

Mr. Daniel D. Jackson has devised an apparatus for the determination of specific gravity which is shown in Fig. 67, and which he describes as follows:[1]

Above is suspended a burette with graduations about 9 inches (23 cm.) long, and with an inside diameter of about ¼ inch (0.6 cm.). This is connected with a glass bulb approximately 5½ iches (13 cm.) long and 1¾ inch (4.5 cm.) in diameter.

The Erlenmeyer flask below is of heavy glass and contains a ground glass stopper, which is hollow, and has a neck of the same bore as the burette. The flask has a capacity of exactly 200 cubic centimeters up to the graduation on the neck of the stopper.

In order that the work may be more rapid, the burette is not graduated in cubic centimeters as in other instruments of this nature, but is made to read directly in specific gravity. The manufacturer of the instrument (Emil Greiner, 78 John Street, New York City), makes the glass bulb of such a size that from the mark on the neck at the top to the mark on the burette just below the bulb, the capacity is exactly 180 cubic centimeters. If 50 grams of cement are taken, this mark represents a specific gravity of 2.50.

200 (Capacity of flask).
—180 Capacity of bulb to 1st graduation.

= 20 Volume displaced by 50 grams of cement.
$50 \div 20 = 2.50$, Specific gravity.

The burette is graduated for every 0.05 in specific gravity and

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[1] *Jour. Soc. Chem. Ind.*, XXIII, No. 11.

five equidistant marks are placed between each of these accurate graduations. In this way the instrument is made to read with accuracy to 0.01 in specific gravity.

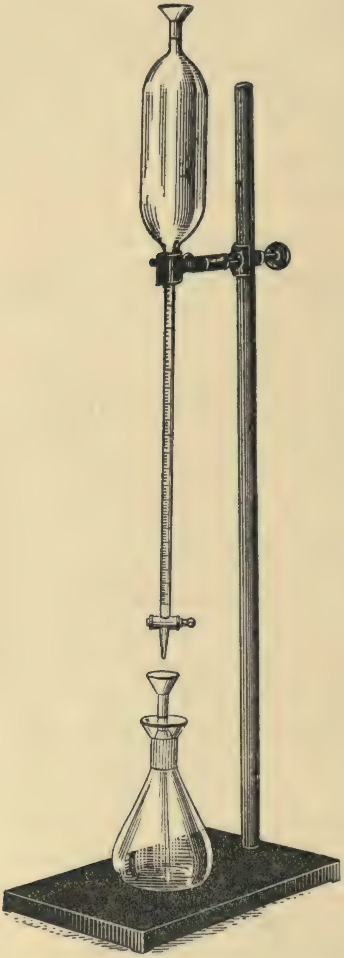

Fig. 67, Jackson's Specific Gravity Apparatus.

The accompanying table gives the calculations used in the original graduation of the instrument:

TABLE XXIII.—FOR GRADUATING JACKSON'S APPARATUS FOR THE DETERMINATION OF THE SPECIFIC GRAVITY OF CEMENT.

Sp. Gr.	Reading. cc.	Displacement.	Sp. Gr.	Reading. cc.	Displacement.
2.50	180.00	20.00	3.01	183.39	16.61
2.51	180.08	19.92	3.02	183.44	16.56
2.52	180.16	19.84	3.03	183.50	16.50
2.53	180.24	19.76	3 04	183.55	16.45
2.54	180.31	19.69	3.05	183.61	16.39
2.55	180.39	19.61	3.06	183.66	16.34
2.56	180.47	19.53	3.07	183.71	16.29
2.57	180.54	19.46	3.08	183.77	16.23
2.58	180.62	19.38	3.09	183.82	16.18
2.59	180.69	19.31	3.10	183.87	16.13
2.60	180.77	19.23	3.11	183.92	16.08
2.61	180.84	19.16	3.12	183.97	16.03
2.62	180.92	19.08	3.13	184.03	15.97
2.63	180.99	19.01	3.14	184.08	15.92
2.64	181.06	18.94	3.15	184.13	15.87
2.65	181.13	18.87	3.16	184.18	15.82
2.66	181.20	18.80	3.17	184.23	15.77
2.67	181.27	18.73	3.18	184.28	15.72
2.68	181.34	18.66	3.19	184.33	15.67
2.69	181.41	18.59	3.20	184.37	15.63
2.70	181.48	18.52	3.21	184.42	15.58
2.71	181.55	18.45	3.22	184.47	15.53
2.72	181.62	18.38	3.23	184.52	15.48
2.73	181.69	18.31	3.24	184.57	15.43
2.74	181.75	18.25	3.25	184.62	15.38
2.75	181.82	18.18	3.26	184.66	15.34
2.76	181.88	18.12	3.27	184.71	15.29
2.77	181.95	18.05	3.28	184.76	15.24
2.78	182.01	17.99	3.29	184.80	15.20
2.79	182.08	17.92	3.30	184.85	15.15
2.80	182.14	17.86	3.31	184.89	15.11
2.81	182.21	17.79	3.32	184.94	15.06
2.82	182.27	17.73	3.33	184.98	15.02
2.83	182.33	17.67	3.34	185.03	14.97
2.84	182.39	17.61	3.35	185.07	14.93
2.85	182.46	17.54	3.36	185.12	14.88
2.86	182.52	17.48	3.37	185.16	14.84
2.87	182.58	17.42	3.38	185.21	14.79
2.88	182.64	17.36	3.39	185.25	14.75
2.89	182.70	17.30	3.40	185.29	14.71
2.90	182.76	17.24	3.41	185.34	14.66
2.91	182.82	17.18	3.42	185.38	14.62
2.92	182.88	17.12	3.43	185.42	14.58
2.93	182.94	17.06	3.44	185.47	14.53
2.94	182.99	17.01	3.45	185.51	14.49
2.95	183.05	16.95	3.46	185.55	14.45
2.96	183.11	16.89	3.47	185.59	14.41
2.97	183.16	16.84	3.48	185.63	14.37
2.98	183.22	16.78	3.49	185.67	14.33
2.99	183.28	16.72	3.50	185.71	14.29
3.00	183.33	16.67			

Method of Determination.—To determine the specific gravity of a cement by means of this instrument:

1. Weigh out accurately to the tenths' place of decimals 50 grams of the dry sample of cement.

2. Fill the bulb and burette with kerosene, leaving just space enough to take the temperature by introducing a thermometer through the neck. Remove the thermometer and add sufficient kerosene to fill exactly to the mark on the neck, drawing off any excess by means of the burette.

3. Run into the unstoppered Erlenmeyer flask about one-half of the kerosene in the bulb. Then pour in slowly the 50 grams of cement and revolve to remove air bubbles. Run in more kerosene until any adhering cement is carefully washed from the neck of the flask, and the kerosene is just below the ground glass.

TABLE XXIV.—CORRECTION IN SPECIFIC GRAVITY IN VARIOUS PORTIONS OF THE GRADUATED SCALE DUE TO CHANGE IN TEMPERATURE, FAHRENHEIT, DURING THE DETERMINATION.

Read the temperature of the oil in the bulb before the determination, and of the oil in the flask after the determination. Add the correction if the temperature of the oil increases, and subtract if it decreases.

Change in Temperature. Fahrenheit.	2.50 to 2.60.	2.60 to 2.70.	2.70 to 2.80.	2.80 to 2 90.	2.90 to 3.00.	3.00 to 3.10.	3.10 to 3.20.	3.20 to 3.30.	3.30 to 3.40.	3.40 to 3.50.
0.5°	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
1.0	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
1.5	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03
2.0	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.05
2.5	0.03	0.04	0.04	0.04	0.04	0.05	0.05	0.05	0.06	0.06
3.0	0.04	0.04	0.05	0.05	0.05	0.05	0.06	0.06	0.07	0.07
3.5	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.08	0.08
4.0	0.05	0.06	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.09
4.5	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.09	0.10	0.10
5.0	0.07	0.07	0.08	0.08	0.09	0.09	0.10	0.10	0.11	0.12
5.5	0.07	0.08	0.08	0.09	0.09	0.10	0.10	0.11	0.12	0.13
6.0	0.08	0.08	0.09	0.10	0.10	0.11	0.11	0.12	0.13	0.14
6.5	0.08	0.09	0.10	0.10	0.11	0.12	0.12	0.13	0.14	0.15
7.0	0.09	0.10	0.11	0.11	0.12	0.13	0.13	0.14	0.15	0.16
7.5	0.10	0.11	0.11	0.12	0.13	0.14	0.14	0.15	0.17	0.17
8.0	0.10	0.11	0.12	0.13	0.14	0.14	0.15	0.16	0.18	0.18
8.5	0.11	0.12	0.13	0.14	0.14	0.15	0.16	0.17	0.19	0.20
9.0	0.12	0.13	0.14	0.14	0.15	0.16	0.17	0.18	0.20	0.21
9.5	0.12	0.13	0.14	0.15	0.16	0.17	0.18	0.19	0.21	0.22
10.0	0.13	0.14	0.15	0.16	0.17	0.18	0.19	0.20	0.22	0.23

4. Place the hollow ground glass stopper in position, and turn

it to fit tightly. Run in kerosene exactly to the 200 cubic centimeter graduation on the neck, making sure that no air bubbles remain in the flask.

5. Read the specific gravity from the graduation on the burette and then the temperature of the oil in the flask, noting the difference betwen the temperature of the oil in the bulb before the determination and the temperature of the oil in the flask after the determination.

TABLE XXV.—CORRECTION IN SPECIFIC GRAVITY IN VARIOUS PORTIONS OF THE GRADUATED SCALE DUE TO CHANGE IN TEMPERATURE, CENTIGRADE, DURING THE DETERMINATION.

Read the temperature of the oil in the bulb before the determination and of the oil in the flask after the determination. Add the correction if the temperature of the oil increases, and subtract it if it decreases.

Change in Temperature. Centigrade.	2.50 to 2.60.	2.60 to 2.70.	2.70 to 2.80.	2.80 to 2.90.	2.90 to 3.00.	3.00 to 3.10	3.10 to 3.20	3.20 to 3.30	3.30 to 3.40	3,40 to 3.50
0.2°	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
0.4	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
0.6	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
0.8	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03
1.0	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04
1.2	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.05	0.05
1.4	0.03	0.04	0.04	0.04	0.04	0.05	0.05	0.05	0.06	0.06
1.6	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.06	0.06	0.07
1.8	0.04	0 05	0.05	0.05	0.06	0.06	0.06	0.06	0.07	0.07
2.0	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.08	0.08
2.2	0.05	0.06	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.09
2.4	0.06	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.10	0.10
2.6	0.06	0.07	0.07	0.07	0.08	0.08	0.09	0.09	0.10	0.11
2.8	0.07	0.07	0.08	0.08	0.09	0.09	0.10	0.10	0.11	0.12
3.0	0.07	0.08	0.08	0.09	0.09	0.10	0.10	0.11	0.12	0.12
3.2	0.07	0.08	0.09	0.09	0.10	0.10	0.11	0.12	0.13	0.13
3.4	0.08	0.09	0.09	0.10	0.10	0.11	0.12	0.12	0.13	0.14
3.6	0.08	0.09	0.10	0.10	0.11	0.12	0.12	0.13	0.14	0.15
3.8	0.09	0.10	0.10	0.11	0.12	0.12	0.13	0.14	0.15	0.16
4.0	0.09	0.10	0.11	0.12	0.12	0.13	0.14	0.14	0.16	0.17
4.2	0.10	0.11	0.11	0.12	0.13	0.14	0.14	0.15	0.17	0.17
4.4	0.10	0.11	0.12	0.13	0.13	0.14	0.15	0.16	0.17	0.18
4.6	0.11	0.12	0.12	0.13	0.14	0.15	0.16	0.17	0.18	0.19
4.8	0.11	0.12	0.13	0.14	0.15	0.16	0.16	0.17	0.19	0.20
5.0	0.12	0.13	0.14	0.14	0.15	0.16	0.17	0.18	0.20	0.21

Make a temperature correction to the reading of the specific gravity by the use of the accompanying tables.

For the convenience of those using the Centigrade thermometer the table of corrections for that instrument has also been compiled.

It is thought possible that the variation in the different brands of kerosene might be sufficient to cause an error in the determination. A collection of various good and bad kerosenes was made and the coefficient of expansion of each sample was determined.

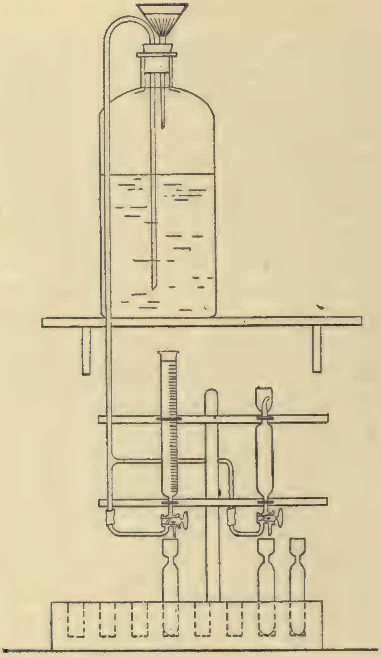

Fig. 68, Simple Apparatus for Specific Gravity.

The differences in expansion found were entirely within the limit of error of the determination.

With the instrument herein described the time required to make a determination is about ten minutes, and the accuracy is to 0.01.

Simple Apparatus for Specific Gravity.

Fig. 68 shows a simple form of apparatus which the writer has usually used for taking specific gravity. It is, of course, not so neat and elegant as the apparatus devised by Mr. Jackson, but it can be made of apparatus found about the laboratory or which can be purchased from the stock of any dealer. Referring to the illustration it will be seen that in place of the special form of burette used in the Jackson apparatus, a 50 cc. automatic pipette and a 25 cc. burette graduated in $^1/_{20}$ cc. and which can be read to $^1/_{40}$ cc. are used. These are mounted on a stand and connected with a reservoir of kerosene on a shelf above. In place of the special flask of the Jackson apparatus a test tube drawn out near its upper end to about ¼ or ⅜-inch in diameter is used. The test tube should be about 8 inches long and 1 inch in diameter, and should hold about 100 cc. It is then drawn out about 6 inches from the bottom and a mark made on the neck by covering the latter with wax, scraping this away, in a ring around the drawn out part, and then moistening this with hydrofluoric acid. Holes about 1½ inches deep and just large enough to hold the tube are then bored in the board, to form a stand for the test tube.

To determine the specific gravity of a cement, dry the tube and run in a pipette full of kerosene. Then fill from the burette to the mark. This will require about 75 cc. or possibly more. Now note the quantity and dry the flask. Again run in a pipette full of kerosene, placing the opening of the pipette well down in the tube so as not to wet the neck of the latter. Now brush into the flask 25 grams of the cement to be tested, after carefully weighing the latter to at least 0.025 gram. The cement should be brushed into the flask very gradually and any particles adhering to the upper part of the tube brushed into the neck. Now add kerosene carefully from the pipette until the mark on the neck is reached. The volume displaced is the difference between this quantity and that required to fill the empty tube; and the specific gravity is the weight in grams, or 25, divided by the volume displaced. For example, if it takes 81.35 cc. to fill the flask to the mark when empty and it takes 73.3 to fill it with the cement, the specific gravity of the latter will be $25 \div (81.35 - 73.3)$ or $25 \div 8.05 = 3.11$. A large number of the tubes can be made and the volume required to fill each etched on with hydrofluoric acid. A dry tube will then always be ready. The cement sample should be weighed out and allowed to stand 15 minutes, on the shelf by the large bottle of kerosene. This avoids the necessity of making corrections for temperature. A table showing the specific gravity corresponding to any displacement, is given below:

TABLE XXVI.—SHOWING CONNECTION BETWEEN DISPLACEMENT AND SPECIFIC GRAVITY.

Displacement. cc.	Specific Gravity.	Displacement. cc.	Specific Gravity.
7.500	3.33	8.000	3.13
7.525	3.32	8.025	3.12
7.550	3.31	8.050	3.11
7.575	3.30	8.075	3.10
7.600	3.29	8.100	3.09
7.625	3.28	8.125	3.08
7.650	3.27	8.150	3.07
7.675	3.26	8.175	3.06
7.700	3.25	8.200	3.05
7.725	3.24	8.225	3.04
7.750	3.23	8.250	3.03
7.775	3.22	8.275	3.02
7.800	3.21	8.300	3.01
7.825	3.20	8.325	3.00
7.850	3.19	8.350	2.99
7.875	3.17	8.375	2.98
7.900	3.16	8.400	2.98
7.925	3.15	8.425	2.97
7.950	3.14	8.450	2.96
7.075	3.13	8.475	2.95

The apparatus must be set in a place free from sudden changes of temperature, and the measuring must be carefully done. The arrangement is well adapted for use where only a few determinations are made each day.

With Specific Gravity Bottle.

Where the apparatus is not at hand for the above methods, the specific gravity may be taken by means of the ordinary specific gravity bottle. First weigh the bottle, empty, then fill the bottle with water and weigh. Then dry and fill with benzine and weigh. Calculate the specific gravity of benzine from the formula

$$x=\frac{B-p}{W-p},$$

where x = sp. gr. of benzine, B = weight of bottle full of benzine, W = weight of bottle full of water, and p = weight of the empty bottle.

Now introduce a weighed portion of the cement into the bottle, fill with benzine, and weigh. The specific gravity of the cement may then be found by the formula

$$X = \frac{C \times x}{B + C - D},$$

where B = weight of the bottle full of benzine, C = weight of the cement. D = weight of the bottle and the cement and the benzine, x = specific gravity of the cement as found above, and X = specific gravity of the cement. Turpentine or paraffin may be used in place of benzine.

OBSERVATIONS ON SPECIFIC GRAVITY.

Test of Little Value Alone.

While a minimum specific gravity clause is a feature of every specification for Portland cement, there is probably no test which taken by itself might lead to more faulty conclusions. The test of itself is designed to detect underburning and adulteration. Unfortunately for any conclusions as to the latter we might draw, low specific gravity is often, and indeed is usually, caused by "aging" of the cement, so that to reject a cement because of a low specific gravity may be to reject it because it has been well seasoned. It is now generally considered that cement is greatly improved by seasoning as the water and carbon dioxide of the air react with any free or loosely combined lime in the cement, which might otherwise cause the latter to be unsound. As the cement absorbs these constituents from the air its specific gravity becomes less and less. This is as it should be, since the specific gravity of calcium carbonate is only 2.70 and that of calcium hydrate only 2.08, and these are the two compounds probably formed during seasoning.

If a sample which has been kept for some time is dried at 100° C., its specific gravity will be found to be higher than it was in the undried condition, but still not as high as when it was freshly made. If this sample is subjected to a strong ignition in a platinum crucible over a good blast lamp, its specific gravity will still further increase and may even be more than the original specific gravity of the freshly made cement, in the case where the latter has been poorly burned. The following specific gravities, determined at different times, of a number of Portland cements, illustrate the above facts.

Sample No.	Specific Gravity.				
	1	2	3	4	5
When made	3.19	3.21	3.16	3.15	3.20
After 28 days, undried	3.11	3.12	3.10	3.09	3.08
After 28 days, dried at 100° C	3.16	3.18	3.14	3.12	3.14
After 6 months, undried	3.08	3.04	3.08	3.03	3.04
After 6 months, dried at 100° C	3.13	3.09	3.12	3.09	3.09
After 6 months, ignited	3.18	3.21	3.18	3.15	3.19

Reference to the above table shows that samples 2, 4 and 5 would have failed to come up to the standard specific gravity specification after six months, and yet, briquettes made of the samples at the same time the specific gravity determinations were made, showed the cement to be at its best, after storage for that length of time.

If the specific gravity of cement is not lowered by storage, no seasoning has taken place, and consequently no benefits have been derived by the cement from aging. Determinations of specific gravity made both on the undried and dried samples of cement may give us an insight into the amount of seasoning the cement has had. If the two results agree closely, it is probable that the cement is fresh, but, if these results vary by 0.05 or more, we may assume that the cement has been in storage for a few weeks at least.

The specific gravity determination is of little value in determining whether cement has been underburned or not. The experienced cement chemist at the mill can see at a glance by looking at the clinker if it is underburned, and the engineer or inspector can judge better by the test for soundness. It is also for the reasons given above, no indication of adulteration. If, however, the specific gravity of a cement is low, it is well to examine it a little more closely, to see if it is adulterated, by the methods outlined under the section on "Detection of Adulteration."

CHAPTER XIV.

FINENESS.

STANDARD SPECIFICATION AND METHOD OF TEST.

Specification.—It shall leave by weight a residue of not more than 8% on the No. 100, and not more than 25% on the No. 200 sieve.

Method of Operating the Test.—*Apparatus.*—The sieves should be circular, about 20 cm. (7.87 ins.) in diameter, 6 cm. (2.36 ins.) high, and provided with a pan. 5 cm. (1.97 ins.) deep, and a cover.

The wire cloth should be woven (not twilled) from brass wire having the following diameters:

No. 100, 0.0045 in.; No. 200, 0.0024 in.

This cloth should be mounted on the frames without distortion: the mesh should be regular in spacing and be within the following limits:

No. 100, 96 to 100 meshes to the linear inch.

No. 200, 188 to 200 meshes to the linear inch.

Fifty gram. (1.76 oz.) or 100 gr. (3.52 oz.) should be used for the test, and dried at a temperature of 100° C. (212° F.) prior to sieving.

Method.—The thoroughly dried and coarsely screened sample is weighed and placed on the No. 200 sieve, which, with pan and cover attached, is held in one hand in a slightly inclined position, and moved forward and backward, at the same time striking the side gently with the palm of the other hand, at the rate of about 200 strokes per minute. The operation is continued until not more than one-tenth of 1 per cent. passes through after one minute of continuous sieving. The residue is weighed, then placed on the No. 100 sieve and the operation repeated. The work may be expedited by placing in the sieve a small quantity of large shot. The results should be reported to the nearest tenth of 1 per cent.

OTHER METHODS.

Methods of Sieving, Sieves, Etc.

Where many sievings have to be made every day, the use of a sieve without top and bottom is the general plan. In this case the sieving is done over a large piece of paper or oil cloth. When it is desired to ascertain if the operation has been completed, the material on the paper is rolled to one side, by lifting the edge of the paper, thus exposing a clean surface over which the sifting may be continued and the amount passing through the sieve observed. An experienced operator will be able to tell, by his eye and sense of time, when the operation is finished, without recourse to balance and weights. In place of striking the sieve against the palm of the hand some operators bounce one side of it, gently up and down, on a small block of wood, taking care not to bounce any of the material over the top of the sieve. The use of shot also greatly hastens the operation of sieving, as the bouncing of these latter, on the wire cloth of the screen, keeps the meshes of the latter open. To separate the shot from the coarse material preparatory to weighing the latter, pass the mixture through a 10 or 20 mesh screen.

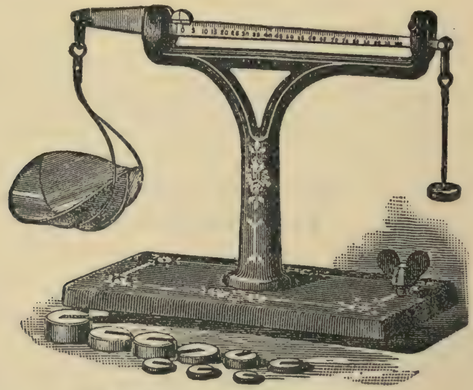

Fig. 69, Balance for Fineness Test.

A convenient balance for use in making sieve tests is shown in Fig. 69. The beam is graduated into $^1/_{10000}$ of a pound, hence if one-tenth pound (= about 45 grams) is taken for the test each of the small divisions on the beam will represent 0.1 per cent. residue.

At the mill where cement is usually tested fresh as it comes from the grinders, it is unnecessary to dry it at 100° C. before making the test, but when inspecting cement which has been stored, it should always be thoroughly dried before making the sieve test. If both specific gravity and sieve tests are to be made, enough cement should be dried for both tests. Descriptions of various forms of drying ovens are given on page 218.

When tests are made by using sieves without a top the sides of these should be high in order to avoid bouncing the material out of the apparatus. If the sieving is done by bouncing the sieve up and down on a block the sides of the sieve should be at least six inches high.

Errors in Sieves.

In purchasing sieves for making the fineness test, care must be exercised to see that they are within the limits prescribed by the standard rules, for there are many so-called standard sieves on the market which are anything but standard. I have seen a No. 100 test sieve bearing the name of a well-known firm, which makes a specialty of supplying apparatus for cement testing, that was made of wire cloth containing, to the linear inch, 90 meshes one way by 93 the other. Not only may standard sieves not contain the proper number of meshes but the wire from which the cloth is woven may be larger or smaller than the size called for in the standard method. This will reduce or increase, as the case may be, the size of the openings of the sieve. Not only may the sieves vary from the standard by reason of incorrect mesh, but also by reason of irregular spacing. That is, the wires may be nearer together in some places than in others, leaving large openings at the latter points for the cement to drop through.

On purchasing sieves they should be examined as to the regularity of the spacing by holding them to the light and also the number of meshes to the inch should be counted. For this latter purpose, small magnifying glasses such as are used for testing linen are convenient. These consist of a small lens, mounted on a stand, in the base of which is an opening exactly one-half inch square. The opening is placed over various parts of the sieve and the number of meshes counted. Where such an instrument is not at hand, an opening of this size may be cut in a piece of cardboard and the meshes counted by the aid of a small reading or pocket magnifying glass. Sieves may also be calibrated by comparing them with other sieves of known value. Any holes or irregularities in test sieves may be stopped up with solder.

OBSERVATIONS ON FINENESS.

Limitations of the Sieve Test.

The fineness to which cement is ground is an important point. Since cement is usually used with sand, the strength of the mortar increases with the fineness of the cement, because the greater is the covering power of the cement, *i.* e., the more parts of cement come into action with the sand. A test for fineness is nearly always included in cement specifications, as the indications from a fair degree of fineness coupled with proper tensile strength, neat, are that the cement will give good results when used with sand.

At the same time the most rigid fineness specification could be filled by a cement which would be many degrees too coarse. Some of the older specifications could be easily filled by a product which would show almost no setting qualities and no sand-carrying capacity. If a sample of clinker is crushed in an iron mortar by a pestle and sieved as fast as it is ground through a 100-mesh screen, a product will be obtained 100 per cent. of which will pass a 100-mesh screen. Many of the older specifications call for only 90 per cent. If a pat is made of this cement it will just about cohere. If, however, the fine particles are sieved through a 200-mesh screen and the flour washed off the coarse particles by benzine and the latter driven off by heat, the product will still all pass a 100-mesh sieve, and yet will have no setting properties. If another sample is ground in a mortar and sieved after every few strokes of the pestle through a 200-mesh screen, it will all pass a 200-mesh sieve and yet will nevertheless be almost worthless as a cement. When washed free from its flour with benzine it will just about hold together. In the writer's laboratory there is a Braun's gyratory muller for grinding samples, in which the grinding is done by an enclosed round pestle revolving in a semi-hemispherical mortar. In the bottom of the mortar is a hole which can be stopped by a plug. The grinding may be done in two ways, one by feeding the sample into the hopper in the cover and allowing it to work its way out at the bottom, then sieving out the fine material from the coarse, and returning the latter through the grinder, and so on until all has passed the sieve. The other, by placing the plug in the bottom of the mortar and allowing the pestle to work upon the material until the latter has reached the desired fineness. Two samples of cement were prepared from the same lot of clinker by these methods. One sample, the one made by passing the clinker through the muller and sieving out the 200-mesh particles after each grind, would, of course, all pass a 200-mesh sieve. The other sample, the one made by grinding the whole sample to the desired fineness without screening, tested 96 per cent. through a 100-mesh sieve and 76.5 per cent. through a 200-mesh sieve. Sand briquettes were made of these two lots of cement with the following results.

Samples made by	7 days. lbs.	28 days. lbs.	3 mos. lbs.	6 mos. lbs.
Grinding and screening to fineness (all 200 mesh)	Broke in clips	Broke in clips	Broke in clips	28
Grinding to fineness without screening	215	295	324	318

The cementing value of Portland cement depends upon the percentage of those infinitesimal particles which we call flour. No sieve is fine enough to tell the quantity of these present. At the same mill it is probable that the sieve test is relative but to the engineer who is called upon to examine the product of many mills using different systems of grinding the sieve test, is hardly to be expected to give the relative percentage of flour in each. The product of the Griffin mill and of the ball and tube mill probably differ much in the percentage of flour present, even when testing the same degree of fineness on the 200-mesh sieve. Even with the ball and tube mill system one ball mill and two tube mills would probably give a product with a higher percentage of flour than one tube mill and two ball mills, even when the cement was ground to the same sieve test. The size screen on the ball mills probably also influences the percentage of flour in a product of a certain fineness.

DETERMINING THE FLOUR IN CEMENT.

A number of devices have been proposed for determining the flour in cement. The chief difficulty with them all seems to be standardization. Each one will give a different result from the other, as we would suppose, for there is no specification as to what is meant by flour, and each apparatus takes out a size different from the other.

Practically all of these forms of apparatus depend upon the suspension of the finer particles of the cement in benzene, kerosene, water, etc. A number of them are described in *The Engineering Record* of August 20th, 1904, page 234. As we have said, the difficulty with all of them is that each would report a different percentage of the cement as flour. Even if they were so calibrated as to give concordant results, these figures would mean nothing more than the sieve test carried a little further. We do not know how fine cement has to be ground in order to "carry sand," although we know that it must be ground considerably finer than merely sufficient for it to just pass the 200-mesh sieve. For experimental purposes it is highly important to obtain some form of apparatus which will enable the finer particles of the cement to be sorted out and graded, in order that the point of fineness at which the sand carrying capacity begins to approach that of ordinary commercial cements may be determined. Such an apparatus, after this point has been determined, would have a practical value, because of two cements the one having the greatest percentage of such "active" particles would be the best ground.

When I have had occasion to desire to know the percentage of fine particles in cement, I have adopted an apparatus modeled after the silt cylinders used for soil analysis. Fig. 70 shows such an apparatus. It consists of a cylinder of at least 300 mm. height and not too great diameter provided with a cork or stopper for closing it and a syphon for drawing off the liquid and suspended matter. The lower end of the syphon is closed by a rubber tube and pinch-cock and the upper one is bent as shown. Strips of paper or file marks are made on the cylinder, one near the top and the other exactly 200 mm. below this one. In use, 100 grams of cement are introduced into the cylinder and the latter filled with benzene to the upper mark and shaken well. It is then placed on a block, the syphon, which should be full of benzene inserted until its opening is level with the lower mark, and exactly 10 seconds after the cylinder was placed on the block the pinchcock is to be opened and the liquid syphoned off to the lower mark. This process is repeated until the liquid above the lower mark settles practically clear in 10 seconds. The residue in the cylinder, or else the suspended matter, is then collected on a filter and its weight determined. From this the percentage of flour is calculated and reported as "particles having a settling value in benzene of less than 20 millimeters per second." These can be again divided into two portions, by allowing 15 seconds to settle, when the value will be 200 ÷ 15 or 13⅓ mm. per second, etc.

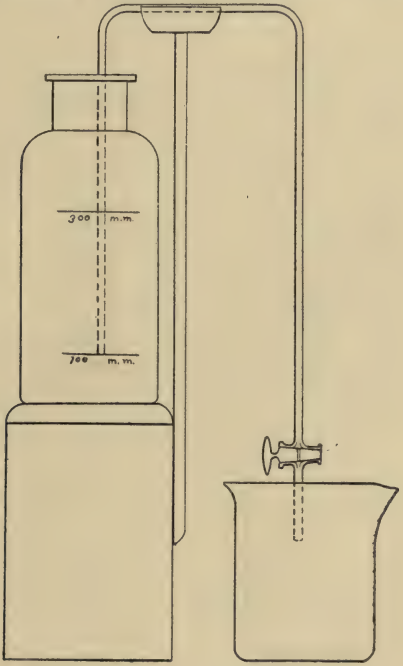

Fig. 70, Apparatus for Determining Flour.

If desired, the size of the largest of these particles can then be measured under the microscope.

If sieves smaller than 200-mesh are desired, it is probable that they could be made by electroplating the cloth of the above size with nickel, silver, etc., and measuring the openings under the microscope, at various stages of the process, until meshes of the proper dimensions are obtained.

CHAPTER XV.

TIME OF SETTING.

STANDARD SPECIFICATION AND METHOD OF TEST.

Specification.—It shall develop initial set in not less than thirty minutes, but must develop hard set in not less than one hour, nor more than ten hours.

Normal Consistency.

Method.—This can best be determined by means of *Vicat Needle Apparatus,* which consists of a frame *(K),* Fig. 71, bearing a movable rod *(L),* with the cap *(A)* at one end, and at the other the cylinder *(B),* 1 cm. (0.39 in.) in diameter, the cap, rod and cylinder weighing 300 gr. (10.58 oz.). The rod, which can be held in any desired position by a screw *(F),* carries an indicator, which moves over a scale (graduated to centimeters) attached to the frame *(K).* The paste is held by a conical, hard-rubber ring *(I),* 7 cm. (2.76 ins.) in diameter at the base, 4 cm. (1.57 ins.) high, resting on a glass plate *(J),* about 10 cm. (3.94 ins.) square.

In making the determination, the same quantity of cement as will be subsequently used for each batch in making the briquettes (but not less than 500 grams) is kneaded into a paste, as described in paragraph 39, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained 6 ins. apart; the ball is then pressed into the rubber ring, through the larger opening, smoothed off, and placed (on its large end) on a glass plate and the smaller end smoothed off with a trowel; the paste, confined in the ring, resting on the plate, is placed under the rod bearing the cylinder, which is brought in contact with the surface and quickly released.

The paste is of normal consistency when the cylinder penetrates to a point in the mass 10 mm. (0.39 in.) below the top of the ring. Great care must be taken to fill the ring exactly to the top.

The trial pastes are made with varying percentages of water until the correct consistency is obtained.

Time of Setting.

Method.—For this purpose the Vicat Needle, which has already been described, should be used.

In making the test, a paste of normal consistency is molded and placed under the rod *(L)*, Fig. 71, as described; this rod, bearing the cap *(D)* at one end and the needle *(H)*, 1 mm. (0.039 in.) in diameter, at the other, weighing 300 gr. (10.58 oz.). The needle is then carefully brought in contact with the surface of the paste and quickly released.

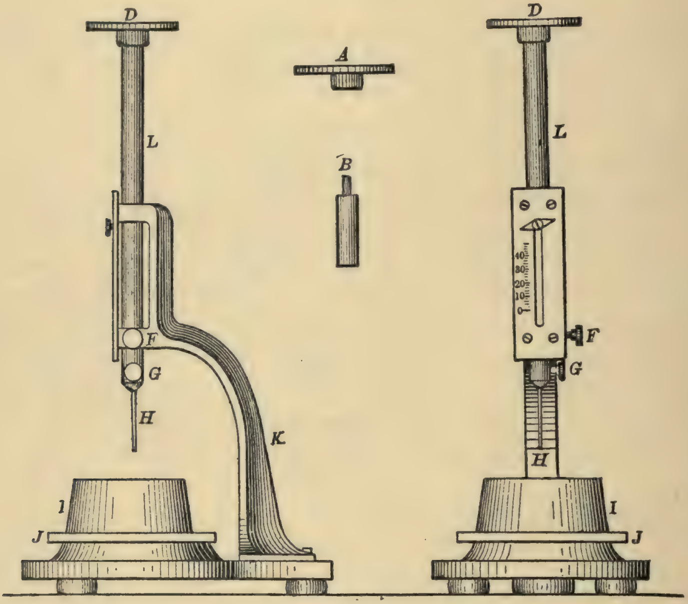

Fig. 71, Vicat Needle.

The setting is said to have commenced when the needle ceases to pass a point 5 mm. (0.20 in.) above the upper surface of the glass plate, and is said to have terminated the moment the needle does not sink visibly into the mass.

The test pieces should be stored in moist air during the test;

this is accomplished by placing them on a rack over water contained in a pan and covered with a damp cloth to be kept away from them by means of a wire screen; or they may be stored in a moist box or closet.

Care should be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point reduces the area and tends to increase the penetration.

The determination of the time of setting is only approximate, being materially affected by the temperature of the mixing water, the temperature and humidity of the air during the test, the percentage of water used, and the amount of molding the paste receives.

OTHER METHODS.

The test proposed by General Gilmore, U. S. A., for determining setting properties is the one most used, however, in this country. It consists in mixing cakes of neat cement from 2 to 3 inches in diameter and ½ inch thick to a stiff plastic consistency and observing the time when they will bear a needle $^1/_{12}$ inch in diameter weighted with ¼ pound. This is noted as the beginning of the set. These pats should be made with a flat top so as not to catch the edge of the needle. Trials are next made every now and then with a $^1/_{24}$ inch in diameter needle weighted with one pound. The time at which the cake is sufficiently firm to bear this latter needle is noted as the end of the set.

The Gilmore needles, or wires, are much more convenient to use where many samples have to be tested, as the pats themselves do not have to be lifted from the moist closet or table, in order to apply the needle. While the Vicat needle unquestionably is a much more scientific instrument and should be used where great nicety is required in making the test, as in settling disputes, etc.; still for ordinary inspection work, where all that is needed is the assurance that the cement will not set before it is laid in position in the job, and that after it is so placed it will harden in a reasonable time, the simpler and less expensive Gilmore needles will answer the purpose just as well as the more expensive Vicat apparatus. The Gilmore needles are the ones generally used by both manufacturers and engineers in determining the setting time of cement, and most of those called upon to test and use cement are familiar with the terms initial, and final set as defined by these needles, so that it does not seem to have been a very wise plan on the part of those formulating the standard rules to recommend that the test be made with the Vicat needle. Setting time is influenced by so many things besides those over which the Vicat needle has control that the personal equation is as much an element in determinations made with this apparatus as with those made with the Gilmore needles.

Fig. 72 shows an arrangement for mounting the Gilmore needles so that they always bear perpendicularly and evenly upon the top of the pat.

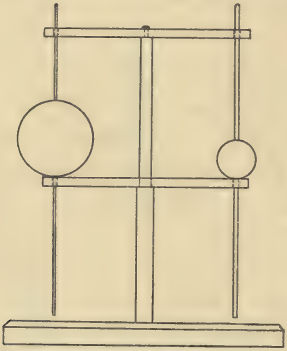

Fig. 72, Gilmore Needles Mounted on Stand.

A simpler form of Vicat needle is that designed by J. W. Bramwell[1]. This apparatus is shown in Fig. 73. It consists of two separate rods, each weighing 300 grams. One of these rods is fitted with a cylinder, one cm. in diameter, which is to be used for determining normal consistency. The other rod is provided with a needle of 1 mm. diameter for the setting time test. The rods are graduated so that the penetration can be read by means of a pointer on the lower guide of the frame. The upper guide is provided with a thumb screw to hold the rods at any height desired and the rods themselves all provided with stops to prevent them from falling and damaging the needle, etc. Whichever rod is not in use is held upright by means of a peg fitting in a hole

[1] Chemical Engineer III, 1, 20.

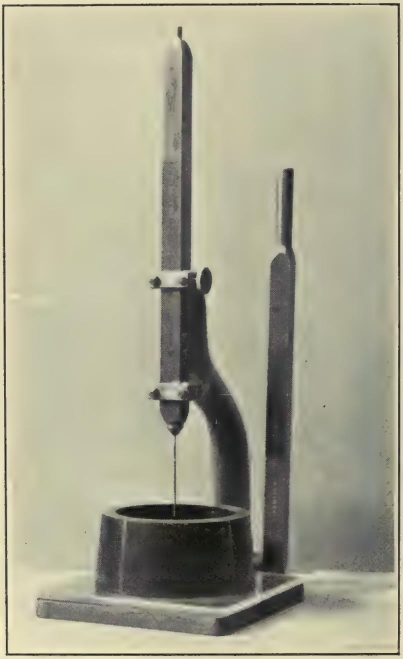

Fig. 73. Bramwell's Improved Vicat Needle.

in the top of the rod, as shown in the illustration. A glass plate and hard rubber ring are also provided with this apparatus, as with the ordinary Vicat needle. One of the noteworthy things about the Bramwell apparatus is its simplicity and low price—about one-half that of the standard Vicat.

The "ball" test for determining the proper consistency is much used in commercial laboratories, using the Gilmore needles to determine set, and in spite of its crudeness, gives results which agree fairly well with those determined by the Vicat apparatus. It consists in forming the mortar into a ball and dropping it from a height of one foot. This fall should not materially flatten nor crack the ball, the former denoting too much water in the mortar and the latter not enough.

When cement sets hard a few minutes after the mortar is mixed it is said to have a "flash" set. Some cements are so quick setting that they even set up under the trowel and on working get dryer instead of more and more plastic.

OBSERVATIONS ON SETTING TIME.

The rapidity with which a cement sets furnishes us with no indication of its strength. The test is usually made to determine the fitness of the material for a given piece of work. For example, in most submarine work a quick-setting cement is desired, that is, a cement which loses its plasticity in less than half an hour, while for most purposes where sufficient time will be given the cement to harden before being brought into use, a slow-setting cement will usually answer better, or one that sets in half an hour or more. The slow-setting cements can be mixed in larger quantities than the quick-setting, and do not have to be handled so quickly, so that for most purposes where permissible they are used.

Factors Influencing the Rate of Setting.

The rate of set is determined by a number of things, chief of which are temperature and the percentage of water used in making the mortar:—The higher the temperature the quicker the set and the larger the percentage of water the slower the set. Temperature has a very marked influence, and many cements which are suitable for use in this country could not be used in the tropics. Similarly in the early spring and late fall when the temperature out of doors is from 20° to 30° F. below that indoors, cement which tests up quick in the laboratory may give perfect satisfaction when used at the outside temperature. This influence is shown by the results given below:

TABLE XXVII.—INFLUENCE OF TEMPERATURE ON THE RATE OF SETTING OF PORTLAND CEMENT.

Temp. °F.[1]	Sample No.	1		2		3		4	
		H.	M.	H.	M	H.	M.	H.	M.
35	Initial set	3	0	5	0	2	0	2	10
	Final set	8	0	10+	..	6	0	6	0
45	Initial set	1	5	3	0	1	15	1	5
	Final set	3	15	7	30	3	30	3	15
60	Initial set	0	30	2	30	0	15	0	3
	Final set	1	10	6	0	1	0	0	10
80	Initial set	0	4	2	00	0	2	..	..
	Final set	0	10	5	30	0	5	..	..
100	Initial set	..	..	0	45	..	..	..	..
	Final set	..	..	3	10	..	..	..	..

The percentage of water used to gauge the pats, or in actual work to make the mortar, effects the setting time, as well as the early strength of the concrete, very greatly. A wet mixture sets very slowly, while a dry one sets much more promptly. In the manufacture of hollow building blocks, where the piece must be removed from the molds at once, only as small a quantity of water as is actually needed to do the work is used, and the mixture of about the consistency of damp sand is rammed into the molds; while in some forms of concrete construction, the mortar is made decidedly plastic, and may be actually poured into the forms. It is then left several days to harden before the latter are removed. Below are given some results on the effects of various percentages of water on the setting time of Portland cement:

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[1] Of room during setting time and of cement and of water used to gauge pats.

TABLE XXVIII.—INFLUENCE OF VARIOUS PERCENTAGES OF WATER USED TO GAUGE THE PATS ON THE SETTING TIME OF PORTLAND CEMENTS.

Percentage of water.	Sample No.	1		2		3		4	
		H.	M.	H.	M.	H.	M.	H.	M.
14	Initial set	0	10	2	10	0	10	0	25
	Final set	2	45	6	0	0	35	0	55
16	Initial set	0	20	2	20	0	10	0	25
	Final set	3	50	6	0	0	35	1	0
18	Initial set	1	5	2	20	0	10	..	35
	Final set	5	0	6	15	0	35	1	15
20	Initial set	2	10	2	40	0	8	1	25
	Final set	6	20	6	15	0	30	4	0
22	Initial set	4	20	3	0	0	5	2	15
	Final set	8	0	6	50	0	30	5	0
24	Initial set	5	10	5	0	0	20	3	0
	Final set	12+	..	8	30	0	50	6	10

Rise in Temperature During Setting.

It was formerly the practice to determine the rise in temperature during setting, any considerable increase being considered as indicative of free lime in the cement, the supposition being that the rise is caused by the heat formed by the hydration of the lime. No conclusion could be more erroneous. From the examination of many samples of Portland cement, every detail of whose manufacture was known, I am not afraid to say positively, that the rise of temperature during setting is not only indicative of free lime, but usually comes from the reverse, not enough lime. Those cements which show the greatest increase in temperature during the process of setting are usually the quick setting cements. These cements usually are low in lime and burned very hard. Many samples of such cements show a rise of temperature distinctly perceptable to the hand, and yet boiling for many hours will fail to disintegrate the pat or warp or check it in any manner. In many instances, the addition of a small quantity (½ per cent.) of finely ground lime or 1 or 2 per cent. of slaked lime will slow the setting of the cement, and in this case no rise of temperature will be met with, showing that the presence of free lime is not the cause of the rise in temperature during setting. On the other hand many samples which fail badly after even a few hours of the steam test, show no greater rise in temperature than the normal. When there is a considerable rise in temperature during the setting of a slow setting cement, something is probably wrong with the cement, but when the rise is met with, in connection with quick set, it is no evidence of free lime, and the conclusion that it is, is unwarranted by facts.

Influence of Sulphates on Setting Properties.

If Portland cement clinker is ground just as it comes from the coolers, without the addition of any foreign substance, the resulting cement is entirely too quick setting to allow of its being properly worked. It is therefore the general practice to either grind a small percentage, usually 2 or 3 per cent., of gypsum with the clinker or else to add to the cement just before it is shipped, a corresponding percentage of finely ground plaster of Paris, in order to regulate the set so as to give time for working, tamping and troweling. At some mills coarsely ground plaster of Paris, or calcined plaster as the manufacturers call it, is added to the clinker before grinding.

Le Chatelier made many experiments on the effect of the addition of gypsum and plaster of Paris to Portland cement. He concluded that the governing action which it exercised over the cement was due to the formation of certain soluble compounds between the sulphuric acid of the calcium sulphate and the very active calcium aluminates of the cement which cause quick setting. He also stated that either gypsum or plaster of Paris could be added to slow the set and that the addition could be made either before or after burning. Since, however, calcium sulphate is decomposed at temperatures decidedly below that at which Portland cement is burned there would be a decided disadvantage, owing to loss of SO_3, in adding gypsum before burning. Indeed from experiments made by the writer if all the sulphur entering the kiln came out with the clinker as calcium sulphate there would be no need to add either gypsum or plaster of Paris.

In spite of Le Chatelier's experiments, it has been the theory generally held in this country that gypsum would not retard the set of cement, but that the only form of sulphate of lime which would do this is plaster of Paris; and that where gypsum is ground in with the clinker, this is transformed into plaster of Paris, the heat generated during grinding being sufficient to drive off the water and make the change from $CaSO_4.2H_2O$ to $(CaSO_4)_2H_2O$. It is true that in many cases the heat generated by the friction of the grinding machinery is sufficient to drive off the water, as the writer has frequently tested cement fresh from the tube mill and found it over 130° C., the temperature at which gypsum loses three-quarters of its water of crystallization. Indeed Shenstone and Cundall state that gypsum begins to lose its water of crystallization at 70° C. in dry air.

To test these various contrary theories and statements the writer and his assistant, Mr. W. P. Gano, carried out the following experiments:[1]

A sample of cement was prepared by grinding fresh normal clinker in the usual way without the addition of any retarder. To separate portions of this were added in different percentages finely ground—

(1) Plaster of Paris, $(CaSO_4)_2.H_2O$, containing 53.18% SO_3.
(2) Gypsum $CaSO_4.2H_2O$, containing 44.32% SO_3.
(3) Dead Burned Gypsum, $CaSO_4$, containing 55.21% SO_3.

The results are given in the tables below:

The first column shows the percentage of gypsum, etc., added to the cement. By percentage is not meant the percentage of gypsum in the mixture, but the percentage of the weight of cement of gypsum which is added. For instance, 2 per cent. means 2 grams of gypsum added to 100 grams of cement, etc.

The second column shows the percentage of water used for the pat, being the amount necessary to obtain a mortar of normal consistency, as determined by the ball test. The third column shows the "initial set" or the time necessary for the cement to harden sufficiently to bear the light Gilmore wire, $^1/_{12}$ inch in diameter, loaded with ¼ pound. The fourth column shows the "final set"

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[1] Meade and Gano, Chemical Engineer, I, 2, 92.

or the time necessary for the cement to harden sufficiently to bear the heavy Gilmore wire, $^1/_{24}$ inch in diameter, loaded with one pound.

TABLE XXIX.—SHOWING THE EFFECT OF PLASTER OF PARIS ON THE SETTING TIME OF CEMENT.

Percentage of Plaster of Paris added.	Percentage of water used to make pats.	Initial set.		Final set.	
		Hours.	Minutes.	Hours.	Minutes.
0	25	0	2	0	6
0.5	23	0	5	0	10
1.0	23	0	50	4	0
1.5	23	2	50	6	0
2.0	22	3	0	6	15
3	22	1	45	5	20
4	22	0	35	4	0
5	22	0	16	2	0
10	22	0	16	1	30
20	22	0	9	0	20

TABLE XXX.—SHOWING THE EFFECT OF GYPSUM ON THE SETTING TIME OF CEMENT.

Percentage of Gypsum added.	Percentage of water used to make pats.	Initial set.		Final set.	
		Hours.	Minutes.	Hours.	Minutes.
1	23	0	2		10
2	23	2	40	5	50
3	22	2	50	5	50
5	22	3	15	6	00
10	22	3	0	5	40
20	22	3	20	6	00

Referring to the tables it will be seen that there is little choice in the three forms of calcium sulphate so far as efficiency goes, all doing the work of retarding the set about equally well. This is to be expected. If the retardation is due to chemical action there is no reason why any one of the three forms should not be as efficient as the others, because they all have approximately the same solubility, that of 1 part in 400-500 parts of cold water. The solution of any of the four would merely be one of a mixture of two kinds of ions, CaO and SO_3, and the SO_3 anions would be as free to react on the aluminates of lime if their source was gypsum as they would if they came from plaster of Paris.

TABLE XXXI.—SHOWING THE EFFECT OF DEAD BURNED GYPSUM ON THE SETTING TIME OF CEMENT.

Percentage of Dead Burned Gypsum added.	Percentage of water used to make pats.	Initial set.		Final set.	
		Hours.	Minutes.	Hours.	Minutes.
1	23	0	6	0	10
2	23	1	45	5	10
3	23	1	47	5	30
5	23	2	0	5	40
10	23	1	50	5	0
20	23	2	20	5	0

It will be noticed, by reference to Table XXIX, that 2% plaster of Paris produced the maximum retardation of the set. Larger quantities than this had the effect of quickening the set of the cement. This maximum of course varies with different cements, but with all it will be found that there is a point beyond which additions of plaster will be attended with shortening instead of further lengthening the setting time of the cement. This phenomena is no doubt due to the fact that plaster of Paris itself is very quick setting. This explanation is strengthened by the fact that the addition of large quantities of calcium sulphate in the other two forms (See Tables II and III), neither of which has any setting properties of its own, does not cause any quickening of the set.

As we have said many manufacturers prefer to add plaster of Paris to cement just before it is shipped. If it is properly mixed with the cement there are certainly points in favor of adding the sulphate here. We do not see, however, why finely ground gypsum would not do the work just as well, saving the cost of calcining. On the other hand if the gypsum is added to the clinker, it is sure to be finely ground and thoroughly disseminated throughout the cement, two things necessary with any form of sulphate, if it is to act as a retarder. There will be no danger of the gypsum failing to do its work, whether the temperature is low or high during grinding, because dehydration is not necessary. It must be remembered, however, that plaster of Paris contains more sulphuric acid than gypsum, 290 parts of the former being equivalent to 344 of the latter or a ratio of 87:100 so that plaster of Paris weight for weight is the more effective of the two. Along this line, dead burned gypsum is still more effective and should be cheaper than plaster calcined by the kettle process.

Influence of Calcium Chloride on Setting Time.

Another substance which will retard the setting of cement is calcium chloride, though the writer has never heard of its being used in practice. Candlot made many experiments upon the effect of chloride of calcium on the setting time of ground cement clinker. Below are some of his results:

TABLE XXXII.—INFLUENCE OF CALCIUM CHLORIDE ON THE SETTING TIME OF PORTLAND CEMENT.

Solution of $CaCl_2$ Gr. per Litre.	1 h. m.	2 h. m.	3 h. m.	4 h. m.
2	0.05	1.05	8.00	1.34
5	0.08	10.00	12.00	2.00
10	8.18	10.00	14.00	5.50
20	1.00	12.00	10.30	8.00
40	4.35	8.00	6.30	8.35
60	3.20	6.00	4.00	6.00
100	0.03	0.20	0.30	3.30
200	0.03	0.09	0.05	0.25
300	0.02	0.08	0.03	0.05

Carpenter[1] also made some experiments on grinding the clinker and calcium chloride together. His results are given below and show that chloride of calcium has effect in retarding the time of setting and exerts the greatest effect when about one-half of 1 per cent. by weight of the chloride of calcium is employed:

TABLE XXXIII.—INFLUENCE OF $CaCl_2$ GROUND DRY WITH THE CLINKER.

Per cent. of $CaCl_2$.	Per cent, of water.	Initial set.	Final set.
0.0	29.8	115	274
0.5	34.1	160	272
1.0	29.8	167	234
1.5	26.4	127	212
2.0	25.4	103	180
2.5	26.4	45	182
3.0	26.4	97	185
3.5	26.4	63	150
4.5	28.6	73	160
5.0	29.8	76	84
5.5	29.8	68	145
6.0	29.8		

Effect of Storage of Portland Cement on Its Setting Properties.

No property of Portland cement is harder to control than its "set," or gives the manufacturer more trouble. This is not so much because of any difficulty in the way of making a slow setting cement, as it is of making one which will stay slow setting under all ordinary conditions of storage and aging. Every manufacturer can cite instances of cement which left the mill having the proper setting time, and yet which turned up at the job with a "flash" set. Bins of freshly made cement will frequently test slow setting and yet, after seasoning some weeks, will show quick set on again testing.

The converse of this is also true, some cements which, when

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[1] Sibley, *Journal of Engineering*, (Cornell Univ.) January, 1905.

freshly made are quick setting, will in time become slow setting, and again slow setting cements may become quick setting and then slow setting again. As a usual rule a cement which is slow setting when freshly made and which becomes quick setting on storage is under-limed, and the trouble can usually be remedied by increasing the percentage of lime in the cement. High limed, well burned and made cements do not usually show this fault. What percentage of lime it is necessary to carry in order to avoid this trouble is a question every mill must decide for itself, but, in general, it may be said that cements high in alumina will require a high percentage of lime to overcome this fault, and in some instances the margin between the minimum of lime to insure against quick set and the maximum allowed by a good hot test is very narrow.

The table below illustrates the changes in the setting time of cement, due to aging.

TABLE XXXIV.—INFLUENCE OF AGING ON THE SET OF PORTLAND CEMENT.

Sample No.		1		2		3		4		5		6		7	
		H	M	H	M	H	M	H	M	H	M	H	M	H	M
Fresh	Initial set	2	50	3	10	4	10	2	40	.	2	.	10	.	4
	Final set	6	0	6	40	8	0	6	15	.	15	.	25	.	10
1 week old....	Initial set	1	30	..	10	2	15	.	3	.	2	.	5	.	4
	Final set	4	10	..	25	6	0	.	8	.	10	.	15	.	10
2 weeks old...	Initial set	0	3	..	5	1	25	.	3	.	15	.	30	.	4
	Final set	0	7	..	11	3	40	.	8	.	35	1	05	.	10
4 weeks old...	Initial set	0	3	..	5	.	30	.	5	1	30	1	50	.	15
	Final set	0	7	..	15	1	50	.	11	4	10	4	45	.	30
3 months old..	Initial set	.	30	..	4	.	10	.	3	1	35	2	0	2	40
	Final set	1	15	..	15	.	30	.	8	4	0	6	10	6	5
6 months old..	Initial set	.	25	..	20	.	..	.	3	2	10	2	0	2	10
	Final set	1	15	1°	10°	.	..	.	8	6	0	6	10	5	40
1 year old	Initial set	.	25	..	55	2	20	.	4	2	0	1	40	2	15
	Final set	1	10	2	30	5	45	.	10	5	30	5	5	6	0

The reason commonly given for the quickening of the set of Portland cement is that the plaster of Paris $(CaSO_4)_2 H_2O$, has hydrated and reverted to gypsum, $CaSO_4.2H_2O$. It is a fact, however, as is generally well known, and as we have mentioned before that gypsum is practically as efficacious a retarder as plaster of Paris. Not only will the mineral gypsum slow the set of cement but the artificial gypsum, formed when plaster hydrates or sets, will also act in the same manner, as the following results will show.

TABLE XXXV.—THE EFFECT OF "SET" PLASTER OF PARIS ON THE SETTING TIME OF CEMENT.

Percentage of "Set" Plaster of Paris added.	Percentage of Water used to make pats.	Initial set.		Final set.	
		Hours.	Minutes.	Hours.	Minutes.
0	25	0	2	0	6
1	23	0	8	0	40
2	23	1	45	5	0
3	23	2	0	5	20
5	23	1	45	6	0
10	23	1	55	5	35
20	23	2	15	5	50

In view of the fact that both gypsum and set plaster of Paris, which is merely plaster of Paris reverted into gypsum, will slow the set of cement, there can be nothing in the theory that plaster loses its control in time over cement, for the only change which the plaster can undergo is to absorb water from the air forming gypsum. We must therefore seek for another solution of the matter. Mr. Clifford Richardson suggested one, in his paper on the "Constitution of Portland Cement," read before the Association of Portland Cement Manufacturers, at Atlantic City, June, 1904. His theory being that the tension in the solid solution of calcium silicates and aluminates, which constitutes cement, is released by changes in temperature, etc., setting free some aluminate which makes the cement quick-setting again.

Against this latter theory are several facts, chief of which is that cements kept in air-tight vessels do not get quick-setting. The writer has many times divided a sample of cement, which from its analysis led him to believe it would develop a "flash" set on aging, into two portions, storing one in a small paper bag and the other in an air tight fruit jar, and, in no case, has he ever observed the sample in the jar to become quick-setting, although in most cases that in the bag developed an initial set of from 2 to 10 minutes after a week's time. In making this test three parts were always made of each sample, both before and after aging, and the bag and jar were placed side by side on the shelf, where both would be subjected to the same changes of temperature, etc.

Influence of Slaked Lime on Setting Time.

Where cement has become quick setting from storage it can generally be made slow setting again by simply adding 1 or 2 per cent. of slaked lime, or by gauging the pat with lime water. This seems to lead to the conclusion advanced by Candlot that the quickening of the set of cement on exposure to air is due to the change of the small percentage of free or of hydrated lime always present in cement to the inert carbonate. This change is brought about by the carbon dioxide of the air, consequently, when not exposed to the air, the cement does not become quick-setting. Slaked lime will not itself slow the setting of unsulphated cement, and calcium sulphate must be present in some form or other, so that it is probably a mixture of calcium sulphate and calcium hydrate which retards the hydration of the aluminates, and consequently the activity of the cement.

Cement which has become quick-setting may also be made slow-setting again by addition of a small percentage of plaster of Paris. One-half of one per cent. is usually sufficient for this purpose. When bins of cement have become quick-setting, from age, it is usual to bring the setting time back to normal by such means. Usually a square box made to hold so much plaster of Paris (when struck off level) is added to every barrow of cement as it is wheeled from the bin to the conveyor, or else a box is dumped into the conveyor at stated intervals of time. The screw conveyor then does the mixing and usually does it pretty thoroughly, too. Some mills are provided with automatic scales and mixers for doing this work, but these are usually installed only in those mills which use plaster of Paris and make the addition before packing, instead of grinding gypsum in with the clinker.

Quick-setting cement may also be rendered slow-setting by mixing them with slow-setting ones, but this must be carefully done to see that both bins are drawn from in the desired proportions.

The property slaked-lime has of slowing the setting time of cement which has quickened with age does not seem to be utilized as much as it might be. I know of one cement mill where slaked lime was added for a short time for this purpose and of another which contemplated doing so. Most manufacturers, however, have found it simpler to add a little more plaster of Paris to such cement as becomes quick-setting, just before it is packed and so bring back its setting time to the normal. The contractor or engineer, however, might in many cases add slaked lime to the cement and so relieve the manufacturer of the expense of taking the cement back to the mill in order to plaster it. On small jobs, where water is added to the concrete from barrels, the addition of a few lumps of lime to the contents of the barrel would make the cement slow-setting, and the resulting concrete would be as strong as if no lime had been added. Sidewalk makers and other users of cement who do not test their purchases may safeguard themselves against using quick-setting cement unawares by the use of lime in this way.

CHAPTER XVI.

TENSILE STRENGTH.

STANDARD SPECIFICATION AND METHOD OF TEST.

Specification.—The minimum requirements for tensile strength for briquettes one inch square in section shall be within the following limits, and shall show no retrogression in strength within the periods specified:[1]

Age.	Strength.
Neat Cement.	
24 hours in moist air	150-200 lbs
7 days (1 day in moist air, 6 days in water)	450-550 lbs
28 days (1 day in moist air, 6 days in water)	550-650 lbs
One Part Cement, Three Parts Sand.	
7 days (1 day in moist air, 6 days in water)	150-200 lbs
28 days (1 day in moist air, 6 days in water)	200-300 lbs

Method of Operating the Test.

Standard Sand.

For the present, the committee recommends the natural sand from Ottawa, Ill., screened to pass a sieve having 20 meshes per linear inch and retained on a sieve having 30 meshes per linear inch; the wires to have diameters of 0.0165 and 0.0112 in., respectively, *i. e.,* half the width of the opening in each case. Sand having passed the No. 20 sieve shall be considered standard when not more than 1 per cent. passes a No. 30 sieve after one minute continuous sifting of a 500-gram sample.

The Sandusky Portland Cement Company, of Sandusky, Ohio, has agreed to undertake the preparation of this sand and to furnish it at a price only sufficient to cover the actual cost of preparation.

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[1] For example the minimum requirement for the twenty-four hour neat cement test should be some value within the limits of 150 and 200 pounds, and so on for each period stated.

Form of Briquette.

While the form of the briquette recommended by a former committee of the Society is not wholly satisfactory, this committee is not prepared to suggest any change, other than rounding off the corners by curves of ½ in. radius, Fig. 74.

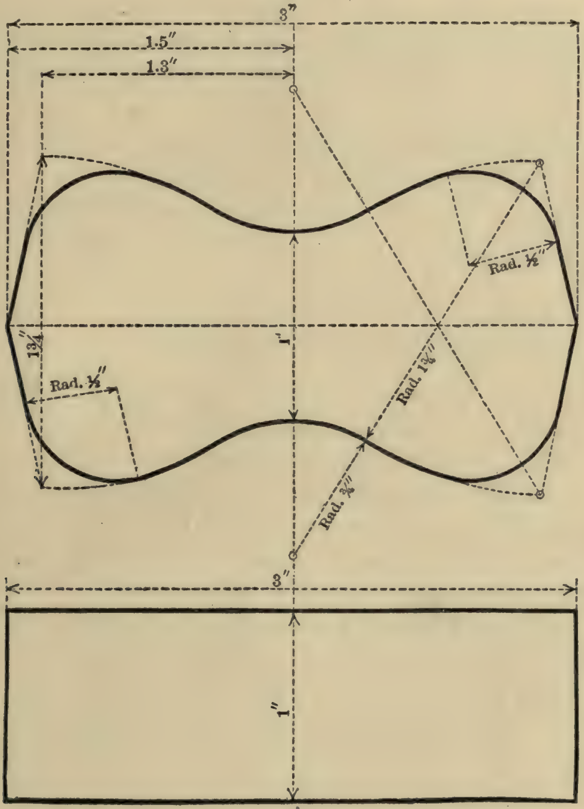

Fig. 74, Standard Form of Briquette.

Molds.

The molds should be made of brass, bronze or some equally non-corrodible material, having sufficient metal in the sides to prevent spreading during molding.

Gang molds, which permit molding a number of briquettes at one time, are preferred by many to single molds; since the greater quantity of mortar that can be mixed tends to produce greater uniformity in the results. The type shown in Fig. 75 is recommended.

The molds should be wiped with an oily cloth before using.

Mixing.

All proportions should be stated by weight; the quantity of water to be used should be stated as a percentage of the dry material.

The metric system is recommended because of the convenient relation of the gram and the cubic centimeter.

The temperature of the room and the mixing water should be as near 21° C. (70° F.) as it is practicable to maintain it.

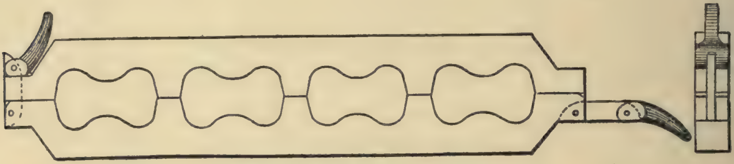

Fig. 75, Gang Mold, Lever Clamp.

The sand and cement should be thoroughly mixed dry. The mixing should be done on some non-absorbing surface, preferably plate glass. If the mixing must be done on an absorbing surface it should be thoroughly dampened prior to use.

The quantity of material to be mixed at one time depends on the number of test pieces to be made; about 1,000 gr. (35.28 oz.) makes a convenient quantity to mix, especially by hand methods.

Method.—The material is weighed and placed on the mixing table, and a crater formed in the center, into which the proper percentage of clean water is poured; the material on the outer edge is turned into the crater by the aid of a trowel. As soon as the water has been absorbed, which should not require more than one minute, the operation is completed by vigorously kneading with the hands for an additional 1½ minutes, the process being similar to that used in kneading dough. A sand-glass affords a convenient guide for the time of kneading. During the operation of mixing, the hands should be protected by gloves, preferably of rubber.

Moulding.

Having worked the paste or mortar to the proper consistency it is at once placed in the molds by hand.

Method.—The molds should be filled at once, the material pressed in firmly with the fingers and smoothed off with a trowel without ramming; the material should be heaped up on the upper surface of the mold, and, in smoothing off, the trowel should be drawn over the mold in such a manner as to exert a moderate pressure on the excess material. The mold should be turned over and the operation repeated.

A check upon the uniformity of the mixing and molding is afforded by weighing the briquettes just prior to immersion, or upon removal from the moist closet. Briquettes which vary in weight more than 3 per cent. from the average should not be tested.

Storage of the Test Pieces.

During the first 24 hours after molding, the test pieces should be kept in moist air to prevent them from drying out.

A moist closet or chamber is so easily devised that the use of the damp cloth should be abandoned if possible. Covering the test pieces with a damp cloth is objectionable, as commonly used, because the cloth may dry out unequally, and in consequence the test pieces are not all maintained under the same conditions. Where a moist closet is not available, a cloth may be used and kept uniformly wet by immersing the ends in water. It should be kept from direct contact with the test pieces by means of a wire screen or some similar arrangement.

A moist closet consists of a soapstone or slate box, or a metal-lined wooden box—the metal lining being covered with felt and this felt kept wet. The bottom of the box is so constructed as to hold water, and the sides are provided with cleats for holding glass shelves on which to place the briquettes. Care should be taken to keep the air in the closet uniformly moist.

After 24 hours in moist air the test pieces for longer periods of time should be immersed in water maintained as near 21° Cent. (70° Fahr.) as practicable; they may be stored in tanks or pans, which should be of non-corrodible material.

Tensile Strength.

The tests may be made on any standard machine. A solid metal clip, as shown in Fig. 76, is recommended. This clip is to be used without cushioning at the points of contact with the test specimen. The bearing at each point of contact should be ¼ in. wide, and the distance between the center of contact on the same clip should be 1¼ ins.

TABLE XXXVI.—PERCENTAGE OF WATER FOR STANDARD MIXTURES.

Neat.	1–1	1–2	1–3	1–4	1–5
18	12.0	10.0	9.0	8.4	8.0
19	12.3	10.2	9.2	8.5	8.1
20	12.7	10.4	9.3	8.7	8.2
21	13.0	10.7	9.5	8.8	8.3
22	13.3	10.9	9.7	8.9	8.4
23	13.7	11.1	9.8	9.1	8.5
24	14.0	11.3	10.0	9.2	8.6
25	14.3	11.6	10.2	9.3	8.8
26	14.7	11.8	10.3	9.5	8.9
27	15.0	12.0	10.5	9.6	9.0
28	15.3	12.2	10.7	9.7	9.1
29	15.7	12.5	10.8	9.9	9.2
30	16.0	12.7	11.0	10.0	9.3
31	16.3	12.9	11.2	10.1	9.4
32	16.7	13.1	11.3	10.3	9.5
33	17.0	13.3	11.5	10.4	9.6
34	17.3	13.6	11.7	10.5	9.7
35	17.7	13.8	11.8	10.7	9.9
36	18.0	14.0	12.0	10.8	10.0
37	18.3	14.2	12.2	10.9	10.1
38	18.7	14.4	12.3	11.1	10.2
39	19.0	14.7	12.5	11.2	10.3
40	19.3	14.9	12.7	11.3	10.4
41	19.7	15.1	12.8	11.5	10.5
42	20.0	15.3	13.0	11.6	10.6
43	20.3	15.6	13.2	11.7	10.7
44	20.7	15.8	13.3	11.9	10.8
45	21.0	16.0	13.5	12.0	11.0
46	21.3	16.1	13.7	12.1	11.1

	1 to 1	1 to 2	1 to 3	1 to 4	1 to 5
Cement	500	333	250	200	167
Sand	500	666	750	800	833

Test pieces should be broken as soon as they are removed from the water. Care should be observed in centering the briquettes in the testing machine, as cross-strains, produced by improper centering, tend to lower the breaking strength. The load should not be applied too suddenly, as it may produce vibration, the shock from which often breaks the briquette before the ultimate strength is reached. Care must be taken that the clips and the sides of the briquette be clean and free from grains of sand or dirt, which would prevent a good bearing. The load should be applied at the rate of 600 lbs. per minute. The average of the briquettes of each sample tested should be taken as the test, excluding any results which are manifestly faulty.

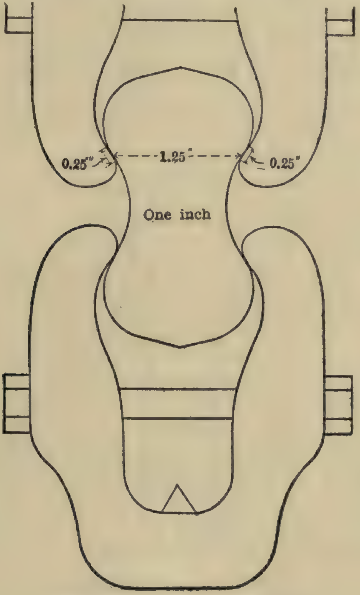

Fig. 76, Standard Form of Clip.

OTHER METHODS.

Standard Sand.

Up to the adoption of the above standard rules, crushed quartz such as is used in the manufacture of sand paper, was considered the standard sand, having been recommended by a former committee of the American Society of Civil Engineers. Indeed, it is probable that it is still used in by far the greater number of testing laboratories in the country. As this sand is a commercial product it can be obtained in large quantities and of standard grades. The crushed quartz should be of such size that it will all pass a No. 20 sieve and yet be retained upon a No. 30.

Where the value of the cement is desired with regard to some particular piece of work, the sand used for the test may be the sand that is to be used for the work. In this case it is the mortar that is tested rather than the cement. Just as a series of tests made with a standard sand and various brands of cement would give the comparative value of the cements, so a series of tests with an established brand of cement and various sands will give the comparative value of the sands.

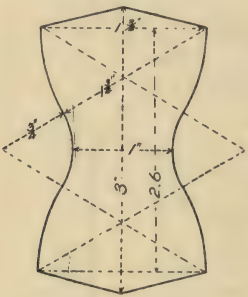

Fig. 77, Old Standard Form of Briquette.

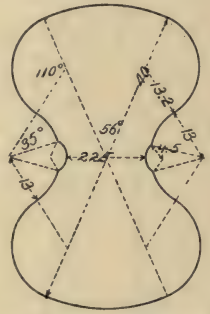

Fig. 78, German Standard Form of Briquette.

Cement, when tested with the natural Ottawa sand, usually shows a greater strength than when tested with crushed quartz. In the case of 7 day breaks, the higher figure may be as much as 40 per cent. of the lower. The reason[1] for this difference is due to the shape of the sand grains. The Ottawa sand being round, it compacts much more closely and has a lower percentage of voids than crushed quartz, as the latter has sharp and angular grains, which mass and wedge, leaving more space between the sand particles.

Forms of Briquettes.

Fig. 77 shows the form of briquette recommended in the report of a former committee on a uniform system for tests of cement

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[1] Brown, Proceedings of Am. Soc. for Test. Mat., IV., (1904), 124.

of the American Society of Civil Engineers,[1] which is similar to the present standard except that the latter has rounded corners. Fig. 78 shows the form recommended by the Association of German Cement Makers, which is the standard in Germany. The dimensions of the two forms are given in the drawings. As will be seen, the weakest section of briquettes of either form is at the center and is one inch in cross-section, in the case of the United States standard; and 5 square centimeters in that of the German. Comparative tests show the American standard to give the higher result of the two. In the case of briquettes of neat cement, this difference amounts sometimes to as much as 30 or 40 per cent. of the lower.

The briquettes to be broken at the expiration of twenty-four hours are made of neat cement, that is, cement alone, while those to be broken only after the lapse of seven days or longer, should be made both of neat cement and of a mixture of one part cement to three parts sand.

Molds.

The various kinds of molds, other than the standard form, used in this country for making briquettes, are shown in Figs. 62, 63 and 79. They are usually made of gun metal, brass, or some alloy of copper that does not easily rust on exposure to moisture. They are made in two pieces to facilitate the removal of the briquette after molding. When in use the two sections are held together by means of a lever clamp, or a clamp provided with a thumb-screw, or by a spring. Preference is usually to be given to the clamp rather than to the spring, as the latter is likely to give a little during the ramming of the mortar into the mould, allowing the mould to spread, which would result in a distorted briquette, and an enlarged breaking section.

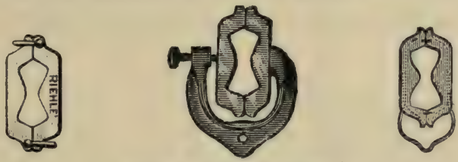

Fig. 79, Form of Molds.

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[1] This committee presented its report at the annual meeting of the society, January 21, 1885, and was then discharged.

Fig. 80 shows another form of gang mold. If a hole is bored through from side to side of this mould, between the third and fourth openings, so as not to interfere with the briquettes, and a bolt provided with a thumb-screw is run through this the mould will be considerably stiffened thereby and springing will be guarded against.

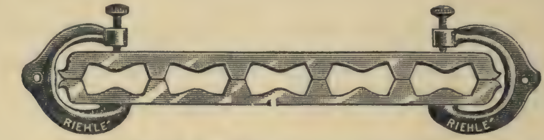

Fig. 80, Gang Mold, Screw Clamp.

To clean the molds, lay them all flat on the table without the clamps just as if briquettes were to be made and scrape off any hardened cement with a piece of sheet zinc or other soft metal. Then brush off with a stiff bristle brush and wipe with a piece of oily waste. Turn the molds over and repeat the process on the other face. Now separate the molds and place the halves in a long line with the mold part forming a trough, brush with a stiff brush and wipe off with oily waste. Briquettes should not be allowed to become too hard before removing from the molds. For most cements, if briquettes are made in the morning, they can be removed from the molds in the afternoon, and the molds cleaned at once before the cement hardens.

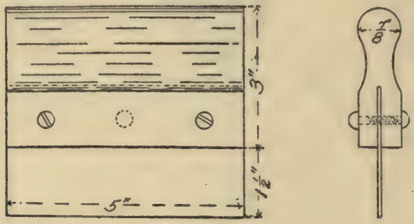

Fig. 81, Scraper for Cleaning Molds.

Fig. 81 shows a scraper for cleaning molds. This consists of a block of wood 5x3 inches, rounded to form a handle, into which is fixed a piece of zinc.

Mixing.

In place of a glass plate, a sheet of brass ⅛-inch thick makes an excellent mixing surface. Slate and soapstone slabs are also used. Both, however, absorb water and draw it away from the briquettes. This can be avoided by keeping a damp cloth over that part of the table used for mixing when not in service. Or melted paraffin may be poured over the heated slab and allowed to soak in and the whole then cooled. The excess of paraffin is, of course, to be scraped off with a metal scraper.

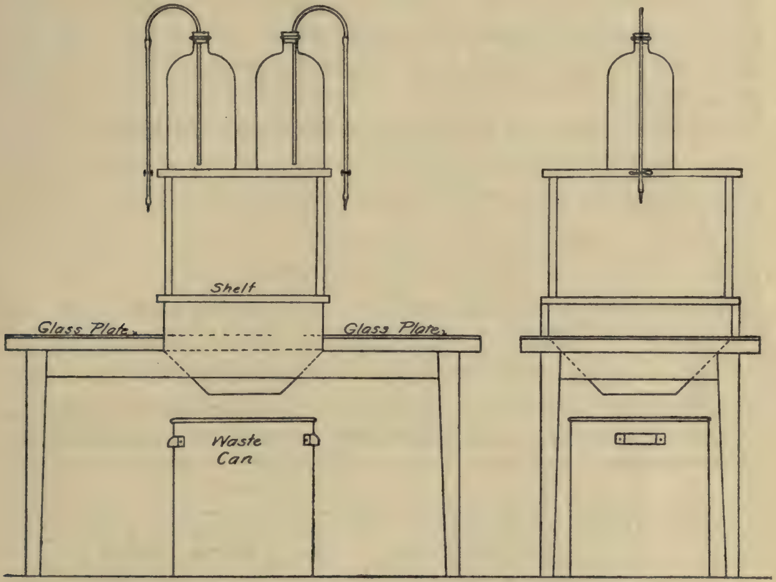

Fig. 82, Table for Mixing Mortar and Making Briquettes and Pats.

Fig. 82 shows a convenient table for mixing mortar and making briquettes and pats. It consists of a table arranged with glass or brass plates or slate slabs at either end and the central part of the table raised four or five inches above the ends as shown. The space between the shelf and the glass plate is left open so that the surplus mortar, etc., used in making a set of briquettes may be swept through this and into a waste-can placed below. A piece of tin bent to form a trough, as shown, conducts the waste into the can. Above the first shelf, which is used for the scales, measuring cylinders, pat glasses, etc., a second shelf is supported by four uprights—one at each corner. At each end of this shelf are to be placed 2-gallon bottles provided with siphons of glass and rubber, as shown. These siphons are closed by pinch-cocks, as shown. Drawers may be placed in the front of the table for holding such articles as trowels, spatulas, etc. Four 2-gallon bottles should be provided, and while two are in use on the table the other two should be full and standing nearby to get the room temperature.

Instead of kneading the cement mortar with the hands as prescribed by the standard rules, the larger number of testers use a trowel, working the mortar back and forth on the table,under the trowel.

Percentage of Water.

The percentage of water used in gauging the mortar for the test pieces has a considerable influence on the strength of the cement. This is shown by the table given below which is taken.

TABLE XXXVII.—INFLUENCE OF VARIOUS PROPORTIONS OF WATER ON THE NEAT STRENGTH OF PORTLAND CEMENT. (E. S. LARNED).

Cement Brand.	Water Per cent.	Tensile Strength.					
		24 Hours.	7 Days.	28 Days.	3 Months.	6 Months.	12 Months.
Giant Portland.	15	371	655	875	941	720	787
	16	303	750	973	1008	735	816
	18	260	649	773	831	645	748
	20	233	500	693	716	621	676
	22	184	546	636	658	601	589
	24	167	539	649	644	629	755
Atlas Portland.	13	366	775	859	1067	892	832
	14	404	780	891	972	852	781
	16	363	602	725	844	806	723
	18	308	570	723	785	728	724
	20	225	590	718	760	674	636
	22	116	554	649	731	643	604
	24	42	510	691	695	632	574

from a paper by Mr. E. S. Larned[1] on this subject. It will be noticed that in the case of both cements, the dryer mixtures give the higher results. This is probably due to the fact that the dry mixtures require hammering or ramming to get them in the molds, while the wet mixtures were merely forced in with the thumb as they were too soft for this treatment. Other experimenters, however, have found results differing in some particulars from Mr. Larned, and while agreeing with him that the dryer mixtures give higher short time tests, their experiments show the differences on long time tests to be slight and usually in favor of the wet mixtures. This has also been the writer's experience, but in his case both the dry and the wet mixtures were merely pressed into the molds with the thumbs.

Storage of Briquettes.

The briquettes may be placed in water either flat or on edge. The latter gives more surface exposed to the water. The tanks in which the briquettes are immersed may be made of galvanized iron and of any desired size. They are usually, however, from two to three inches deep. Where space is limited, they may be placed one above the other on a suitable framework.

When much testing has to be done, a good form of trough for the storage of briquettes is made of stout two-inch board lined with sheet zinc. These troughs may be placed one above the other on a suitable wood frame. A small stream of water should be kept running through them all the time. This can be done by arranging overflow tubes so that the water will flow from the upper trough into the next one below, etc.

In the writer's laboratory, the briquette trough is placed in the cellar and is made of concrete. It is raised about 2 feet from the floor and is 8 inches deep. The water level is maintained at about 6 inches. The temperature of this cellar is very even both in summer and winter. In making the trough, a very dense concrete was used so as to be sure of no leakage from it into the cellar.

After the briquettes have attained their initial set they should be marked with an identifying number by a steel die and dated

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[1] Proceedings, Amer. Soc. Test. Mat., III., (1903), 401.

as shown in Fig. 83. The marking should always be done in the corners and never across the breaking section. Sand briquettes may be marked by putting a thin layer of neat cement about $^1/_{16}$ inch thick on one end and marking this. The usual plan, however, is only to mark the neat briquettes and store the sand briquettes with these, in the trough, in such a manner as to make identification possible. When briquettes are only to be made for short periods a pencil may be used for marking, but where long time tests are made steel dies should be used.

In storing the briquettes in the troughs, it will be found most convenient to put all the briquettes to be broken in 7 days, in order of making, in one part of the trough, and those for 28 days in another, etc. The briquettes may be placed edgewise, in pairs, one on top the other; and where the sand briquettes are not marked, it will be found a good plan to place the neat briquettes over the corresponding sand ones.

Fig. 83, Marked Briquette.

The number of briquettes to be made, and the time when these are to be broken, will vary with circumstances. Usually, in permanent laboratories, briquettes are made to be broken at periods of 24 hours, 7 days, 28 days, 3 months, 6 months, 1 year, 2 years, 5 years and 10 years. Usually from 3 to 5 briquettes, both sand and neat, are broken at each period, except at 24 hours, when only neat briquettes are broken. In temporary laboratories, however, the long time tests are, of course, omitted. Three neat and three sand briquettes are usually considerd enough to test the strength of cement at any period, though in some laboratories only two of each kind are broken.

The briquettes should always be put in the testing machine and broken *immediately* after being taken out of the water, and the temperature of the briquette and of the testing room should be constant, between 60° and 70° F. Seven days neat briquettes kept in the room and allowed to dry out for 24 hours before breaking, in many instances, break at less than half the strain of those kept in water the full period. Sand briquettes, however, seldom show any very marked difference.

Testing Machines.

The Fairbanks cement testing machine is much used for cement testing because of its simplicity and automatic action. It is shown in Fig. 84. It consists of a cast iron frame A, made in one piece with a shot hopper B. To this frame are hung the two levers D and C. From the end of the upper lever the weight is applied by allowing shot to flow from the hopper into the bucket F. The tension is applied to the briquettes held in the clips N and N by means of the lower lever C. The lower clip is attached, by means of a ball joint, to a screw with a hand wheel, for lowering or raising, when putting in the briquette and taking up the slack. There is also a counterbalance E, for bringing the levers

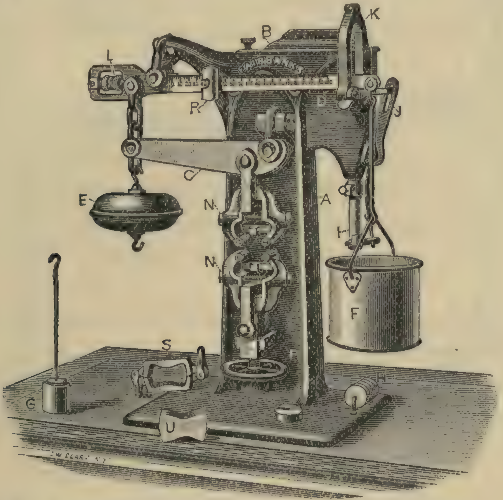

Fig. 84, Fairbank's Automatic Cement Testing Machine.

and bucket into partial equilibrium so that the final adjustment can be made with the ball L. The shot hopper is provided with a lever and gate J, which cuts off the shot as soon as the specimen breaks. The shot is weighed by hanging the bucket on the opposite end of the lever D, by means of a sliding poise R.

To operate the machine:

Hang the cup F on the end of the beam D as shown in the illustration. See that the poise R is at the zero mark, and balance the beam by turning the ball L.

Fill the hopper B with fine shot, place the specimen in the clamps N N, and adjust the hand wheel P so that the graduated beam D will rise to the stop K. Open the automatic valve J so as to allow the shot to run slowly into cup F. When the specimen breaks, the graduated beam D will drop and automatically close the valve J.

If the elasticity of the cement is such that the specimen will not break before the beam strikes the valve, it will be necessary to stop the flow of shot and readjust the hand wheel. This can best be done by lifting the end of the beam against the stop by hand and tightening the hand wheel to hold the beam firmly in position. The shot is then allowed to run until the specimen breaks.

Remove the cup with the shot in it, and hang the counterpoise weight G in its place.

Hang the cup F on the hook under the large ball E, and proceed to weigh the shot in the regular way, using the poise R on the graduated beam D, and the weights H on the counterpoise weight G.

The result will show the number of pounds required to break the specimen.

The flow of shot can be regulated by the cut-off valve.

In breaking a specimen in the above form of the Fairbanks machine, it is necessary to screw the clips up tight before allowing the shot to run into the bucket, in order to guard against having to do this later on in the breaking. This "initial load" which with neat briquettes may amount to at least 400 lbs., has been given as one of the chief objections to this machine. The manufacturers, however, have placed on the market a new machine in which the hand wheel is replaced by a gear, which is actuated by a worm, which in turn is moved by a crank in front of the machine. This does away with the initial strain.

The Riehlé machine (Fig. 85) has all the weight upon one long graduated beam. The load is applied to the briquette by means of the lower hand wheel which actuates a worm gear, while the beam is kept in balance by a weight which is moved along the beam on a carriage by the upper hand wheel. The upper lever serves as an indicator. In testing a briquette both wheels must be moved simultaneously so that the indicator vibrates in the center of the gate. In testing with this machine, the briquette is placed in the grips, and, being carefully adjusted, the hand wheel connected to the lower grip, is turned from left to right, and continued until the indicator of weighing beam (which moves in a gate at the top of the machine and nearly on a line with the

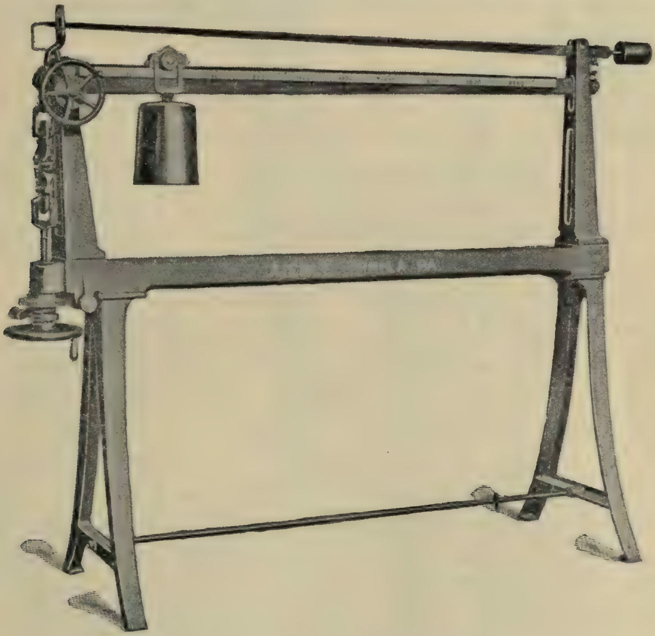

Fig. 85, Riehlé Cement Testing Machine.

eye of the operator) drops. This indicator moves the reverse of the weighing beam, and when too much strain is exerted it falls, and when too much weight is applied it raises to the top of the gate. It is important that the indicator should vibrate in the center of the gate, and rest neither up nor down. This result can be attained by carefully manipulating the large hand wheel and the simultaneous movement of the poise on the weighing beam. When the indicating beam drops down, when the test first begins, the rest of the test can usually continue without again moving the large hand wheel, which is shown underneath the end of the shelf. As is readily understood, the operator propels the poises backward and forward by means of the hand wheel (at butt end of weighing beam) and cord passing around a pulley at the other end of the machine. By a little practice a person gets very expert, and can make a test with facility.

Whichever machine is used the load is to be applied at the rate of 400 pounds per minute.

Neither of these machines is free from sources or error. In the Fairbanks machine there is an error due to the fact some time (in which shot is falling into the bucket) is taken by the beam to fall to the valve checking the shot stream; even then, there is a stream of shot extending from the valve opening to the surface of the shot in the bucket which must fall into the latter and be weighed as part of the load which broke the specimen, though this shot was not in the bucket when the specimen broke. In the Riehlé type of machine, there is an error due to the fact that the chain is attached to the poise at a point not on a line with the knife edges of the beam, giving the poise a tendency to lift up or pull down.

To avoid the initial strain to which a briquette broken on the Fairbanks, or other automatic testing machines of this type, is subjected, the Olsen Automatic Cement Testing Machine was designed. In this machine the initial load is avoided by an ingenious arrangement consisting in balancing a bucket of shot against a weight, and then applying the load by allowing the shot to run out of the bucket. Fig. 86 shows the machine.

Referring to the cut, it will be seen that the load is applied through a system of levers by means of the weight shown on the extreme right. Before starting a test this weight is counter-balanced by shot held in the kettle. To make the test the valve in the bottom of this kettle is opened, and as the shot escapes, its equivalent of the weight on the right-hand end of the beam acts on the briquette. At the instant the briquette breaks the escaping stream of shot is cut off by the closing of the valve in the bottom of the kettle, by the upper grip striking the horizontal arm which extends just above it, and thus releasing the curved arm carried on the spindle immediately to the left; this curved arm in turn striking the valve and closing it. The briquette having broken, it only remains to weigh the amount of shot that has escaped from the pan and multiply it by the proper factor to give the load per

Fig. 86, Olsen Automatic Cement Testing Machine.

square inch to which the briquette has been subjected. The machine is furnished with a spring balance on which is placed the pan into which the shot falls. The dial of this spring balance is graduated so as to read in terms of pounds to the square inch on the specimen. It follows that as the test proceeds, the operator can watch the application of the load, and knows at any instant exactly what load is on the briquette. When the briquette breaks, the load which broke it is read at a glance, and jotted down without further manipulation or calculation.

Mr. Arthur N. Johnson, highway engineer of the Maryland Geological Survey, has devised a novel and ingenious cement testing machine[1] which he thus describes:

"The apparatus consists of three parts, a cylinder, A, with a movable piston and filled with water or some other liquid; a cylinder, B, with elastic sides which is connected with the cylinder carrying the piston, and a pressure gauge, C, connected with the other two cylinders. The piston which moves in the cylinder, A, is attached to a threaded rod working through a nut at the top of the cylinder; thus the motion of the piston can be regulated to a nicety. When the piston descends, the pressure developed within the apparatus is registered by the gauge. The pressure forces the water into the middle cylinder, tending to swell the elastic portion of it, at B, which is an India rubber tube.

"If a ring of any material is slipped over the cylinder, B, so that the rubber sides are confined, a pressure will be exerted against the inner side of the ring, when the piston in the cylinder, A, is pushed down, which will be registered in pounds per square inch by the gauge. For testing cement, cylindrical rings of rectangular section are made. These rings, one of which is in position at R, are put over the center cylinder, after which a bell-shaped cap, D, is placed upon the test ring and is held in place by a nut, E,which is screwed lightly against the cap. If this nut were not used the rubber tube in expanding would tend to raise the cap and the rubber would be forced between the cap and the cement ring, which would result in bursting the rubber tube. When a cement ring has been put in place the piston is screwed down by

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[1] *Engineering Record*, (1903), XLVIII. **20**, 602

means of a handle, F. This causes the rubber tube to swell, pushing it against the inner side of the cement ring. A uniform pressure is thus secured over the entire inner surface of the cement ring, and, up to the moment of rupture, every section of the ring is under exactly the same stress, assuming that the walls of the rings are everywhere of equal thickness. It is also evident that all rings of the same size are subjected to exactly the same conditions so far as the application of the pressure is concerned, and the difference in the pressures at which different rings are ruptured must be occasioned by a corresponding difference in the strength of the rings. In other words the apparatus treats every test specimen exactly alike, not subjecting one to different stresses from

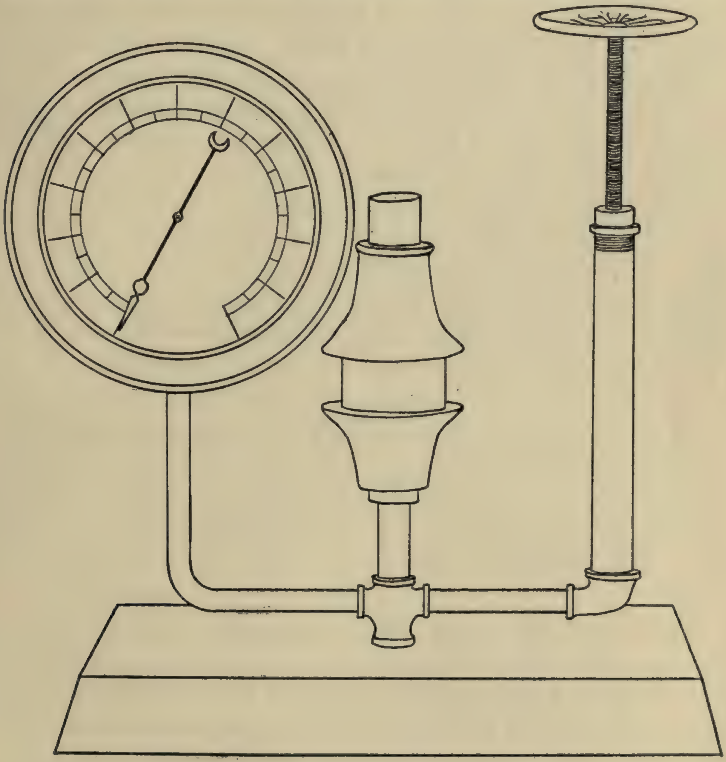

Fig. 87, Johnson's Cement Testing Machine.

another as is the case with the usual method of making tensile tests of cement. It is also practically impossible for any shock to be given to the specimen while under stress on account of the air which is enclosed within the apparatus acting as a cushion.

"So far experiments have been carried on with rings made in two ways, cutting them with a diamond drill from a solid slab of cement mortar which has set the proper time and also by moulding in moulds. Both methods are successful with neat cement, but mortars composed of sand and cement could not be successfully drilled with the style of drills at hand. Another feature noticed in connection with drilling cement rings was the lack of uniformity in the size of the rings, so that it was necessary to measure each section in order to determine the results. No such difficulty, however, has been experienced in moulding rings. In order to have them fit in the testing machine it will sometimes be necessary to grind the ends of the rings so that they will present flat surfaces. It is very easy to do this and the amount or grinding required seldom takes over one or two minutes. This precaution is necessary to prevent the rubber tube from blowing out between the test specimen and the brass caps which inclose it."

To do away with the personal equation in the breaking of the briquette, Prof. J. M. Porter, Professor of Civil Engineering in Lafayette College, has designed an ingenious form of cement-testing machine. In breaking a briquette with this machine, the attention of the operator is not required after the proper adjustment of the test-piece in the clips. He describes his machine as follows:[1]

The load is applied by water flowing into a tank suspended from the long arm of a very sensitive 15 to 1 lever. The weight of the lever and tank is counterbalanced by an adjustable weight on the left. Water is admitted to the tank from a large reservoir on the roof under a practically constant head of 90 feet, so there is no sensible variation of pressure in the stream admitted through a carefully fitted gate valve in the supply pipe. The position of this valve at "on," "off," and all intermediate points is shown by an index attached to the stem of the valve and register-

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[1] *Engineering News*, March 7, 1895.

ing on a dial marked off with the number of pounds per minute applied to the specimen as determined and verified by previous experiment.

When the briquettes break, the lever drops a few inches, then the plunger at the right end of the lever enters the pneumatic stop, and the lever and tank are gradually brought to rest. During the fall of the tank and before it comes to rest, a chain attached to the end of the valve stem in the tank is brought into tension and arrests the descent of the valve before its seat stops descending. The opening of this valve allows the contents of the tank to be quickly discharged into a hopper placed upon the floor, and is then carried off through a waste pipe to the sewer. As soon as the tank has discharged its contents, the weight on the left end of the lever brings the lever and tank into the position, the valve taking its seat during this movement and the machine is ready for another break. The actual load can be applied at from 0 to 80 pounds per minute, thus giving an increase of stress of, from 0 to 1,200 pounds per minute. The speed generally used is 400 pounds per minute, and with the valve set for this speed the needle beam will float every time within 1/5 second of the proper time.

The stress on the specimen is measured by a poise traveling on a graduated scale beam, which can be read by means of a vernier to 1 pound and can be moved automatically or by hand at the wish of the operator. The automatic movement is accomplished by the following described device:

The horizontal disk and its engaged friction wheel are driven continuously by the pulley placed at the lower end of the vertical shaft and belted to overhead shafting. This friction wheel is feathered to a sleeve that runs loose on its shaft and carries a coned clutch that is nominally disengaged from its cone, which is also feathered to the shaft, and can be moved slightly longitudinally on the shaft into contact with the clutch by the action of the vertical lever.

When the needle beam rises, it makes contact through a vertical pin in the top of the frame, which completes an electric circuit and sends a current through the electro-magnet and causes it to attract its armature at the lower end of the vertical lever, which, moving to the right, engages the friction clutch and causes the shaft to revolve. This shaft operates the sprocket wheel and chain, which draw out the poise on the scale beam until the needle beam drops, breaking the electric circuit. Breaking the electric circuit releases the armature and allows the friction clutch to disengage and the poise comes to rest. The friction wheel may be set at a greater or less distance from the center of the disk by turning the capstan head nut, and the chain is overhauled faster or slower, causing the poise to move accordingly. If desired, the poise may be operated by the hand wheel without interfering with the automatic device other than cutting out the circuit. The chain is attached to the poise in line with the three knife-edges of the scale beam, hence the tension in the chain has no tendency to lift up or pull down the poise. This point is often overlooked in designing this detail, not only in cement machines, but in testing machines in general. The writer has a cement machine in which the error due to this cause is over 15 pounds.

Clips.

Some of the various forms of clips are shown in the following illustrations. Fig. 88 shows that recommended by the former committee of the American Society of Civil Engineers. This form does not seem to be very satisfactory as the bearing surface is insufficient and the briquette is likely to break from the crushing of its surface at the point of contact. The new clip Fig. 76 on page 321, is much more to be preferred. It affords sufficient bearing surface without binding. Various authorities at different times have advocated cushioning the grips by placing blotting paper between the jaw of the grip and the briquette, or stretching rubber

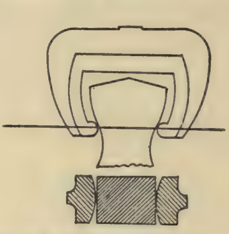

Fig. 88, Old Standard Clip.

bands around the jaws, so as to soften the point of contact of these with the test piece. Mr. W. R. Cock[1] has devised the use of a rubber bearing as shown in Fig. 89. In this clip the line of contact between the grip and the briquette is a rubber tube mounted on a pin. These tubes are readily replaced for a few cents when worn out. Adjustable and roller clips are also upon the market and seem to give satisfaction. In order that the stress upon the briquette shall be along the proper lines great care must be exercised in properly centering the briquette in the clips, and the form of the latter must be such that it does not clamp the head of the briquette thus preventing the test piece from adjusting itself to an even bearing. At the same time the surface of contact must be sufficient to prevent the briquette from being crushed at this point. Striking the happy medium has so far proved not any too easy. The clips are usually suspended by conical bearings which permit them to turn so as always to transmit the stress in a direct line btween the bearings.

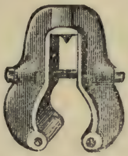

Fig. 89, Rubber Cushioned Clip.

Lack of Uniformity in Tensile Tests.

In cement testing, the personal equation enters very largely into the results. In a paper[2] by Prof. James Madison Porter, of Lafayette College, he gave a series of results upon the same cement by nine different operators, tested by the method of the Society of Civil Engineers as they understood it. The results varied from 75 to 247 pounds per square inch. The first Committee on a Uniform System for Tests of Cement of the American Society of Civil Engineers, in their report, says:

> "The testing of cement is not so simple a process as it is thought to be. No small degree of experience is necessary before one can manipulate the materials so as to obtain even approximately accurate results.
>
> "The first test of inexperienced, though intelligent and careful persons,

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[1] *Engineering News*, Dec. 20, 1890.

[2] *Engineering News*, March 7, 1895.

are usually very contradictory and inaccurate, and no amount of experience can eliminate the variations introduced by the personal equations of the most conscientious observers. Many things, apparently of minor importance, exert such a marked influence upon the results, that it is only by the greatest care in every particular, aided by experience and intelligence that trustworthy tests can be made."

The personal equation probably plays its most important part in the gauging of the cement, the making of the mortar, and the molding and breaking of the briquettes. In order to eradicate these variations of treatment, machines have been introduced upon the market to do the work automatically and so do away with whatever variations the operator may introduce into the hand work, principally among which are the *Steinbrüch* and the *Faija mixers* and the *Bohme hammer.*

Machines for Mixing the Mortar.

The *Steinbrüch* mixer, (Fig. 90), is much used in Germany and gives good results; the chief objection to its universal adoption in this country is its cost, about $130. It consists of a circular shell having on its upper side, near the outer edge a groove or trough in which the mortar is mixed. A wheel, whose rim corresponds with the groove in the pan, rests in this trough and re-

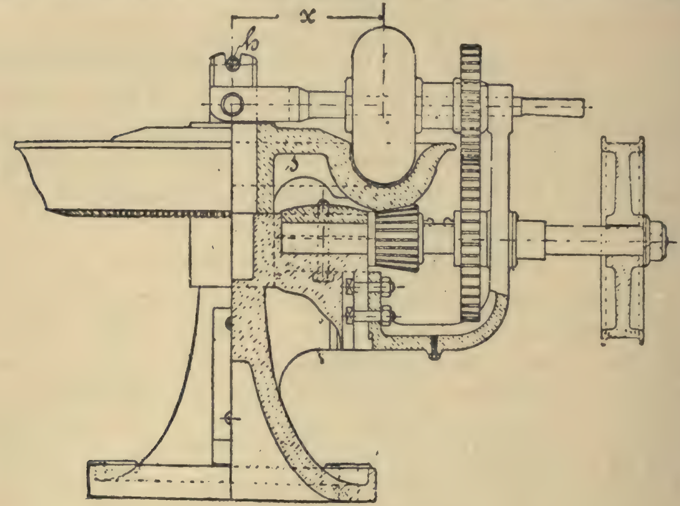

Fig. 90, Steinbrüch Mixer.

volves around a fixed horizontal axis, which is above and normal to the axis of the pan. The pan is now made to revolve about its vertical axis, and at the same time the wheel is made to revolve about its horizontal axis, along with the pan and at the same rate of speed, by means of gearing. The mortar is thus rubbed between the outer rim of the wheel and the inner surface of the trough. Small plows scrape the mortar from the sides of the trough, as the latter revolves, thus keeping the mortar in the bottom of the trough and under the wheel. When the mixing is complete, which according to the German rules requires two and one-half minutes, the wheel and plows, the axes of which are hinged, are lifted from the trough and the mortar taken out. The apparatus appears unnecessarily complicated, and its seems as if a simpler and less expensive form might be devised and used to advantage.

The Faija mixer is the design of the late Henry Faija, of England. Fig. 91 shows the mixer as made by Riehlé Bros. Testing Machine Co., of Philadelphia. It consists of a circular pan of about one foot in diameter, within which revolve the arms of a stirrer. These arms revolve around their own axis in one direction and around the pan in the reverse direction. This motion is given them by a fixed internally toothed wheel which actuates the pinion of the stirring spindle. To operate, first find by means of a trial test by hand gauging the proper proportion of water to ce-

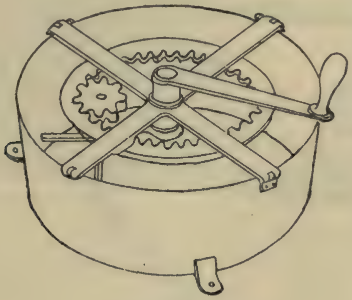

Fig. 91, Faija Mixer.

ment. Next place in the mixer sufficient cement to fill a gang of molds and add at once the proper quantity of water for this weight of cement. Then turn the handle of the machine fairly quickly for from a half to three-quarters of a minute, when it will be found that the cement and water are thoroughly mixed and ready for the molds. In gauging cement and sand in this machine, first mix the cement and sand dry and then add the water, etc.

Machines for Molding the Briquettes.

The Bohme hammer consists of a tilt hammer with automatic action. The hammer is thus described by Max Gary:[1] "The hammer is driven by a cam wheel of ten cams actuated by simple gearing. The wrought-iron handle of the hammer is let into the

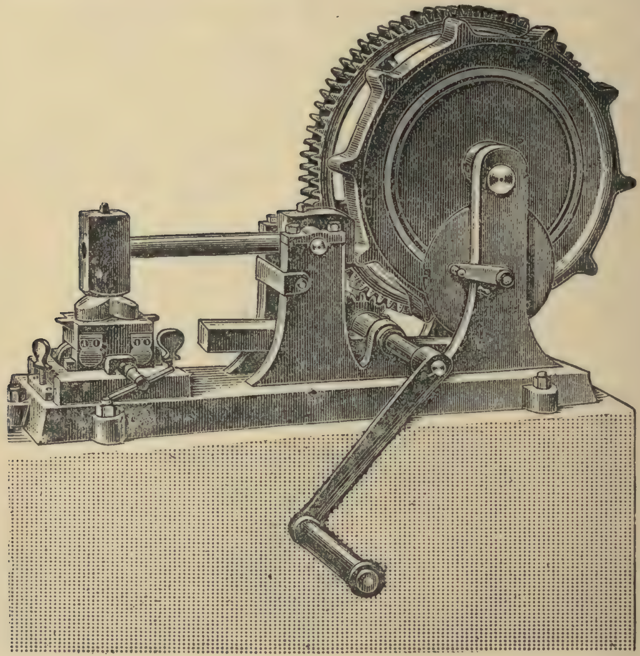

Fig. 92, Bohme Hammer.

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[1] Trans. Am. Soc. C. E., 30, 1.

cross-head which carries the axle of the hammer and keyed to this cross-head and to the cap so that it may be replaced if worn. The steel hammer weighing 4½ pounds, is similarly fastened to the cap. As soon as the intended number of blows has been delivered, the mechanism is automatically checked, the proper setting having been made for this purpose before beginning the work." (The number of blows required in the German Standard test is 150).

"The forms to receive the mortar consist of a lower and upper case held together by springs. The lower case for compression specimens consists of two angle irons held on a planed plate by a grinding strip and a screw acting on the latter. Upward motion is prevented by two wedge-shaped surfaces. The lower case and half the upper one is filled with the mortar to be tested and a plate laid upon its surface. On this plate the blows are delivered. It is of vital importance that the apparatus rests upon a firm non-elastic foundation; preferably it should be placed and fastened on a pier of masonry."

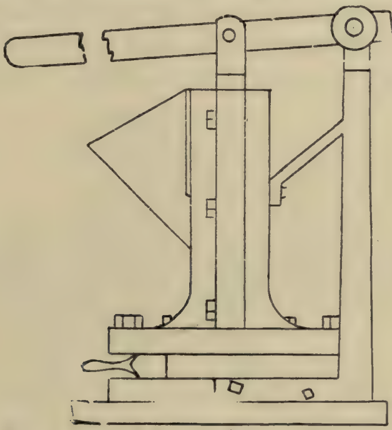

Fig. 93, Jameson Briquette Machine Elevation.

Prof. Charles D. Jameson describes, in his book on Portland cement, a form of machine in use in his laboratory at the University of Iowa. The main portion of the machine consists of a cylinder (Figs. 93 and 94) which is flanged at the lower end, this flange corresponding in shape and size to the upper part of the base. The cylinder is bolted to the base by four bolts, each bolt provided with a filler that holds the lower face of the cylinder 1 inch above the base plate. Both of these faces are accurately planed. It is between these two planed faces that the molding plate swings, the fillers on the bolts acting as stops. The cylinder is made in two parts, bolted together. The bore is the size and shape of the briquette. In this bore works a solid plunger of the shape of the bore. The length of the plunger is sufficient to cover the feed hole when at its lowest point. The plunger is connected to the lever by the connecting rod. The molding plate swings in such a manner that when at either extreme, one of the openings is directly beneath the bore of the cylinder, while the other is directly over the extractor. These extractors are of the

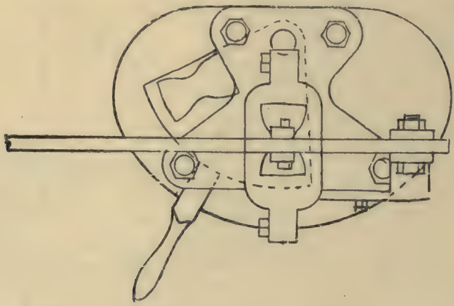

Fig. 94, Jameson Briquette Machine, Plan.

shape of the opening in the molding plate are are raised by levers. When the extractor is at its lowest point its top is a little below is to force the briquette from the mold. On the outside of the cylinder is the hopper.

The method of operation is as follows: The piston is raised until it is above the feed hole, and the cement or mortar in the hopper is forced into the cylinder. The molding plate is pushed against one of the stops so as to bring one of the openings under the cylinder bore. The lever is forced down causing the plunger to force the cement or mortar into the opening in the molding plate. The molding plate is then swung against the other stop. the lower side of the molding plate. The object of the extractors This movement cuts off the briquette and places it directly over the extractor. The other opening in the molding plate is directly under the cylinder bore. The extractor is raised by its lever, and the briquette forced out and removed. The extractor is lowered, the main plunger forced down again, the molding plate swung and another briquette made. The cylinder holds sufficient motar for three briquettes. It should then be filled again. In the machine as described there is no way of regulating the amount of pressure. Experiments made by Prof. Jameson, however, indicate that there is no necessity of this, probably from the fact that the actual pressure is so great under all circumstances that the actual variation forms but a small percentage of it, not sufficient to vary the results.

Aiken's Method of Making Briquettes.

Mr. W. A. Aiken[1], inspector of materials, New York Rapid Transit Co., proposes the following method for minimizing the personal equation in the mixing and moulding of briquettes:

"The gang moulds are filled with dry cement in three layers, the lower two being tamped by three blows of a wooden mallet and a tamping iron exactly fitting the moulds, the top layer being simply put into place, pressed in and smoothed off with a small trowel, after the moulds have been filled. Three blows of the mallet were adopted because repeated experiments demonstrated that this number gave results, when the briquettes were broken, approximating the strength desired in what was considered the most acceptable cement at the 7-day period; fewer blows not giving such satisfactory results in every way, more blows developing abnormal strength at that period as well as at later stages.

"After the briquettes are finished, as far as filling the moulds is concerned, the whole is put into storage tanks and there left to take up as much water as required. At the expiration of 24 hours, all the briquettes are ready to be taken from the moulds, when those for the first period are immediately broken and the others stored in tanks. By careful weighing of a great many sets of briquettes it has been ascertained that 22 per cent. of water by weight is taken up during the first immersion."

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[1] Proceedings Amer. Soc. for Test. Mat., 1904.

OBSERVATIONS.

High Tensile Strength of Unsound Cements.

Perhaps the results of no test are given so prominent a place in the manufacturers' advertisement as the neat strength of briquettes made of his brand. We hear the question constantly propounded by the prospective purchaser of "How much does your cement pull?" and a thousand-pound neat 7-day break is considered compensation for all the deleterious qualities a cement may have. In reality, the neat break is not of so much value as we are apt to suppose, and taken by itself is little criterion of the quality of cement. Unsound cements often give notoriously high results, and the addition of plaster or gypsum will also increase the neat strength. In both of these instances there is apt to be on long time breaks a falling off in strength, permanent in the former case and usually only temporary in the latter case.

This is illustrated by the following table taken from a paper by Mr. W. P. Taylor, on "Soundness Tests of Portland Cement,"[1] read in 1903. This table was compiled from over 200 nearly consecutive tests of a single brand, 100 of them failing in the test and 100 passing.

TABLE XXXVIII.—COMPARISON OF THE TENSILE STRENGTH OF BRIQUETTES PASSING AND FAILING IN THE BOILING TEST.

Age.	Failing.		Passing.	
	Neat.	1 : 3 Sand.	Neat.	1 : 3 Sand.
1 Day	530	...	391	...
7 Days	817	197	643	237
28 Days	749	273	727	303
2 Months	713	274	732	312
3 Months	702	242	749	314

It will be noticed that the early strength of the neat tests of those samples failing to pass the test is much the greater, while the opposite is true of the sand samples.

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[1] Proceedings Amer. Soc. Test. Mat., III. (1903), 381.

Effect of Grinding on Neat and Sand Strength.

A fact that is generally known is that up to a certain point coarse grinding of the cement will give higher neat results than fine grinding. A cement 75 per cent. of which passed a 200-mesh sieve gave after 7 days a neat strength of 912 pounds and a sand strength of 256 pounds. The finer portions of this cement, that passing a 200-mesh sieve, gave for the same period a neat strength of 715 pounds and a sand strength of 463 pounds. A sample of float (i. e., the fine cement dust which collects on the beams, etc., in a cement mill and which is nearly all of it an impalpable powder) gave for 7 days a neat strength of 679 pounds and a sand strength of 558 pounds. This dust mixed with 25 per cent. of coarse cement, i. e., that passing a 100-mesh screen but retained on a 200-mesh, gave 919 pounds neat, but only 252 pounds sand strength in 7 days. Certainly in both these cases neat strength would have given us a poor comparison of the value of the two products. As cement is always used with sand, the sand strength is the important thing.

That the sand strength and neat tests do not necessarily bear any relation to each other, the Table XXXIX will show. The sand strength seems to depend largely upon the fineness, yet different brands of cement giving similar residues on the test sieves will not necessarily show the same relation between neat and sand test. This latter may, of course, be due to differences in the amount of flour, which is not shown by the sieve test, as well as to peculiarities of composition, physical structure, etc., of the clinker from which the cement is ground.

Drop in Tensile Strength.

Another point which has often been brought against cement, and American cements in particular, is that of a permanent drop in tensile strength after the 28-day test. In fairly quick setting cements with their usual low lime content and to which the normal amount of gypsum or plaster has been added, this drop is rarely met with and is probably then due to improper manipulation of the test. In cements high in lime, without being necessarily unsound, or in cements to which a large addition of plaster or gypsum has been made, this drop is often met with. In unsound cements it is usually met with, often after the 7-day test.

It does not necessarily follow that any drop in strength indicates a disrupting action, because as cement briquettes get older they get more and more brittle, and consequently tensile stresses break them more easily. Particularly is this true if the clips exert any twisting action and the load is not very evenly applied. Also cement is never used neat and in the vast majority of cases when a cement shows a slight falling off in neat strength, the sand strength increases with age. This is shown in Table XL. Humphreys states that the compressive strength of neat cement does not experience this drop when the cement is sound even if the tensile strength does fall off somewhat after the 28-day test; an important fact, if true, as cement is seldom if ever used in tension.

TABLE. XXXIX—SHOWING LACK OF ANY RELATION BETWEEN NEAT AND SAND STRENGTH AND FINENESS.

Cement No.	Boiling Test.	Fineness.		Tensile strength, 7 days.		Tensile strength, 28 days.	
		Through No. 100.	Through No. 200.	Neat.	1 : 3.	Neat.	1 : 3.
1	O. K.	99.0	80.0	915	303	1013	353
2	O. K.	99.0	80.0	790	285	853	320
3	O. K.	99.1	85.1	933	298	990	340
4	O. K.	98.8	83.3	930	288	963	330
5	O. K.	94.8	78.8	733	270	825	360
6	O. K.	95.0	79.0	748	280	620	275
7	O. K.	96.5	74.0	818	273	858	360
8	O. K.	97.0	74.0	800	260	1013	280
9	O. K.	95.1	70.0	910	190	1038	266
10	O. K.	95.0	70.0	683	180	750	320
11	O. K.	98.0	82.5	1008	200	1115	282
12	O. K.	97.9	82.5	855	283	970	333
13	O. K.	94.8	75.0	610	350	810	440
14	O. K.	92.0	70.0	544	206	884	261
15	O. K.	93.4	70.4	701	217	893	310
16	O. K.	93.8	74.2	680	359	791	410
17	O. K.	97.1	82.5	855	283	970	333
18	O. K.	97.4	82.7	910	255	970	305

Coarse grinding of the cement has some influence on the increase in strength with age. A very fine cement increases neat very little after 7 days, while a coarser one keeps on increasing. This is no doubt due to the fact that the coarse particles are acted on much slower than the fine ones, and solution and crystallization of these go on after the finer ones are all hydrated. The following experiment was made with the same cement. Cement A is just as it comes from the mills. Cement B is cement A with the coarse particles (residue on a No. 200 sieve, removed):

TABLE XL.—SHOWING LOSS IN STRENGTH OF NEAT BRIQUETTES AND GAIN IN SAND BRIQUETTES AFTER SEVEN DAY TEST.

Cement No.	Boiling Test.	Tensile strength.									
		Neat.					1 : 3 Sand.				
		7 days	28 days	3 mos	6 mos	1 year	7 days	28 days	3 mos	6 mos	1 year
1	O. K.	657	615	650	680	711	240	302	360	381	405
2	O. K.	915	845	730	760	755	310	360	375	378	415
3	O. K.	1058	1023	890	852	783	200	263	425	410	463
4	O. K.	865	727	730	650	728	317	353	390	400	416
5	O. K.	708	656	661	663	665	201	279	402	455	520
6	O. K.	735	704	684	688	658	290	401	426	443	477
7	O. K.	916	845	816	825	802	301	360	424	450	456
8	O. K.	1012	875	890	921	944	306	374	381	410	467
9	O. K.	912	815	826	814	827	292	327	368	381	381
10	O. K.	856	803	810	814	811	275	361	369	391	418
11	checked	1150	775	610	615	674	235	315	366	381	427
12	"	947	816	702	310	Dis.	210	246	247	311	312
13	"	812	304	318	301	204	294	316	321	330	327
14	"	955	811	816	802	503	274	321	375	416	427
15	"	927	802	765	612	344	213	227	264	375	414
16	"	610	314	191	78	95	224	237	241	256	281
17	"	1110	765	342	Dis.	Dis.	275	298	315	362	396

Age.	7 days.	28 days.	3 mos.	6 mos.	9 mos.
Cement A, lbs	618	695	675	725	750
Cement B, lbs	518	546	535	510	549

Of 76 samples of the same brand of cement, each one containing from 63.25 to 63.75 per cent. lime when freshly ground and passing the boiling test, those ground to a fineness of 80-85 per cent. through a No. 200 sieve showed an increase of only 3.4 per cent. neat strength between the periods of 7 and 28 days; while those ground to a fineness of 70-75 per cent. through a No. 200 sieve gained 18.3 per cent. in this time. When a cement gives a high neat break on 7 days, and passes the steam test when received, failure to show an increase in 28 days should not be taken as an indication of a poor cement nor should the cement be rejected because of this. Indeed, if the sand test shows an increase in strength in the 28-day break, the cement should be promptly accepted.

CHAPTER XVII.

SOUNDNESS.

STANDARD SPECIFICATION AND METHOD OF TEST.

Pats of neat cement about three inches in diameter, one-half inch thick at the center, and tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

(a) A pat is then kept in air at normal temperature and observed at intervals for at least 28 days.

(b) Another pat is kept in water maintained as near 70° F. as practicable, and observed at intervals for at least 28 days.

(c) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel for five hours.

These pats, to satisfactorily pass the requirements, shall remain firm and hard and show no signs of distortion, checking, cracking or disintegrating.

OTHER METHODS.

Faija's Test.

Probably the mildest of the hot tests is that of the English cement expert, Henry Faija. His method consists in subjecting a freshly gauged pat upon a plate of glass prepared as directed above to a moist heat of 100° to 105° F. for six or seven hours, or until thoroughly set, and then immersing it in water kept at a temperature of 115° to 120° F. for the remainder of the twenty-four hours. This treatment imparts an artificial age to the cement and quickly brings out any vicious qualities the cement may possess. For this test he uses the apparatus shown in Fig. 95. It consists of a covered vessel in which water is kept at the even temperature of 115° to 120° F. by means of a water-jacket. The inner vessel is filled with water to the height shown. Above the water-level is placed a rack. When the water in the inner vessel is at the temperature of 115° to 120° F. the upper part of the vessel will be filled with aqueous vapor and this latter will be at a temperature of from 100° to 105° F. As soon as the pat is gauged it is put on the rack and left there for six hours. It is then placed in the warm water and allowed to remain eighteen hours longer. The author of the test states that if a test pat after the above treatment shows no signs of cracking or blowing and adheres firmly to the glass plate on which it was made, it may be used with perfect confidence; it will never blow. This test certainly seems fairer to the cement than most of the hot tests, many of which would, if applied to some really good cements, cause them to be rejected.

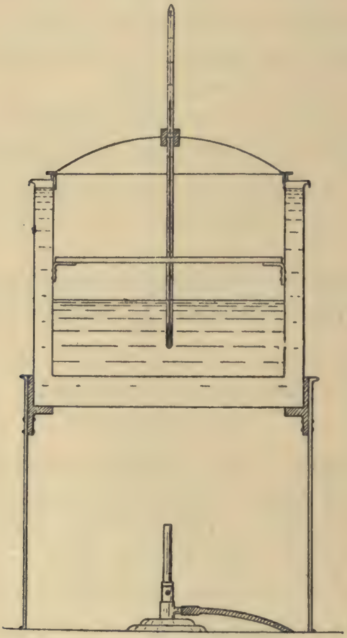

Fig. 95, Faija's Soundness Test Apparatus.

Maclay's Test.

Captain W. W. Maclay modifies this test as follows: Four pats are prepared in the usual manner. One of these pats is placed in a steam-bath of a temperature of 195° to 200° F. as soon as made. The second pat is placed in the same bath as soon as it will bear the one pound wire. The third pat is placed in the steam-bath after double the interval has passed that took the second pat to set hard, counting from the time of gauging. The fourth pat is placed in the steam-bath after twenty-four hours. The four pats are kept in the steam-bath three hours, when they are immersed in water at 200° F. for twenty-one hours each, when they are taken out and examined. All four pats after being twenty-one hours in hot water, should, to pass the test perfectly, upon examination, show no swelling, cracks nor distortions, and should adhere to the glass plates. This latter requirement, while it obtains with some cements nearly free from uncombined lime, is not insisted upon, the cracking, swelling, and distortion being the more important features of the test. Where the cement is very objectionable from excess of free lime the trouble generally shows itself in the cracking or distortion of all four pats. Where the cement is not so bad, the cracking and swelling takes place on the first three pats only. With less objectionable cement only the first two pats crack or swell while the cracking and swelling of the first pat can generally be disregarded.

Captain Maclay does not consider this test final, however, but where the cement fails to pass, gives it another chance by testing briquettes conserved in hot water and comparing with those kept in cold water. He found, in a general way, that the average tensile strength of hot water briquettes of pure cement four days old are nearly as high as the normal seven-day cold, while the hot water seven-day briquettes require nearly the same strain to pull them apart as the normal twenty-eight day cold, when the cement is of good quality. In a poor cement, however, one in which the pats show distortion and cracking, there is generally a marked falling off of the hot water briquettes from the above comparison, and one system can be used to check the other. The briquettes are prepared at the same time the regular cold water test-pieces are made—four additional sets of five each for neat cement and four additional sets of mortar. These are allowed to set twenty-one hours in moist air of about 60° F. They are placed three hours in the steam-bath at 195° F. and then immersed in hot water (200° F.), after which they are broken when two, three, four, and seven days old, respectively, and the breakings compared with the normal breakings of briquettes seven and twenty-eight days old kept in cold water. A more rational test would be a modification of the Maclay test using sand briquettes instead of neat ones.

Kiln Test.

Dr. Bohme suggested the kiln test. The Association of German Cement Makers recommended this test as a means of quickly judging of the quality of a cement, but do not make the test decisive and abide by their twenty-eight-day test on those cements which fail to pass the kiln test. Their method for the test is as follows:

"For making the heat test, a stiff paste of neat cement and water is made, and from this cakes 8 cm. to 10 cm. in diameter and 1 cm. thick are formed on a smooth impermeable plate covered with blotting paper. Two of these cakes which are to be protected against drying in order to prevent drying cracks, are placed after the lapse of twenty-four hours, or at least only after they have set, with their smooth surface on a metal plate and exposed for at least one hour to a temperature of from 110° C. to 120° C. until no more water escapes. For this purpose the drying closets in use in chemical laboratories[1] may be utilized. If after this treatment the cakes show no edge cracks, the cement is to be considered in general of constant volume. If such cracks do appear the cement is not to be condemned, but the results of the decisive test with the cakes hardening on glass plates under water must be waited for. It must, however, be noticed that the heat test does not admit of a final conclusion of the constancy of volume of those cements which contain more than 3 per cent. of calcium sulphate (gypsum) or other sulphur combinations."

Prof. Tetmajer, of Zurich, modifies this method by placing on the bottom of the oven a few millimeters of water. The heat is gradually applied so as to evaporate all the water in from three to six hours; first that on the floor of the oven, and then that absorbed by the mortar. The latter is held on a shelf above the floor. The temperature of the oven remains at about 95° C. until the water is entirely evaporated. After this the heating is contin-

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[1] See page 218.

ued half an hour longer in such a manner as to raise the temperature of the oven to 120° C. This will bring the temperature of the interior of the briquette at a little over 100° C. It is difficult to obtain comparative results by this method as the heat is not the same for all specimens, since after the evaporation of the water, the heat is much greater at the bottom than at the top of the oven.

Boiling Test.

This test, also devised by Prof. Tetmajer, is very similar to the one just given. It consists in rolling a ball of mortar and then flattening the ball to the thickness of half an inch. The consistency of the mortar should be such that it shall neither crack in flattening nor run at the edges. These pats are placed in a vessel of cold water immediately after gauging and heat applied and regulated so that the water boils in about an hour. The boiling is continued for three hours, when the pats are removed and examined for checking and cracking. Many operators after steaming the pats for five hours as prescribed by the standard rules and noting the results place the pats down in the water and boil for from three to five hours.

Calcium Chloride Test.

Candlot discovered by a series of experiments upon cement that if the cement is either gauged with or kept in water containing calcium chloride the free lime in it is slaked much more quickly. The more concentrated the solution the more marked the effect. The action of the salt is, therefore, similar to that of heat, to increase the chemical action causing expansion. If the cement is guaged with a concentrated solution of calcium chloride, the lime will probably all be slaked before the cement sets, so that no cracking will occur on hardening, even if much free lime is present. If, however, the calcium chloride solution is more dilute (40 grams to the liter) it will only cause slaking of a very small percentage of the free lime, such a small percentage as is unobjectionable in cements. If a pat made of this mortar is then kept in a calcium chloride solution of the same strength, the slaking of the rest of the lime will be greatly hastened and crackling will soon appear if a harmful quantity of free lime is present. To carry out the test, gauge the cement with a 4 per cent. solution (40 grams to the liter) of calcium chloride, make into pats upon glass plates and allow to set, after which immerse the pats in the cold 4 per cent. solution of calcium chloride for twenty-four hours and then remove and examine for cracks, softening, etc.

Bauschinger's Calipers.

The expansion or contraction of cement during hardening may be measured directly and very accurately by means of Baushinger's caliper apparatus (Fig. 96). By means of this instrument changes in the length of small parallelopipedons, 100 mm. long and 5 sq. cm. cross-section, may be actually measured to within $^1/_{200}$ mm. The apparatus consists of a stirrup-shaped caliper, having a fine micrometer screw on its right arm, the left being the support of a sensitive lever. The shorter arm of this lever terminates in a blunt caliper point and is pressed against the measuring screw by a spring attached to the long arm. The calipers are readily moved in any direction and the micrometer is read in the usual manner. One revolution of the screw equals 0.5 mm. and the readings on the head are made at $^1/_{200}$ mm. The specimen is molded with square cavities in the end, and in these are set plates

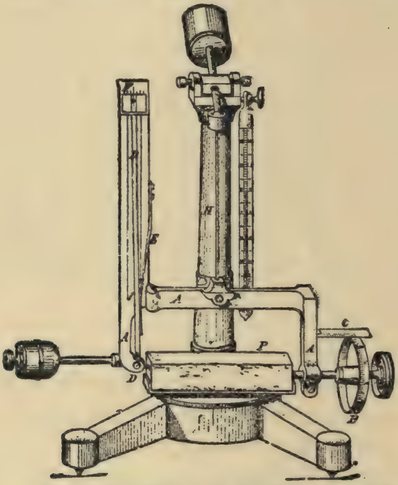

Fig. 96, Bauschinger's Caliper Apparatus.

of glass containing centers for the caliper points. The molding is done similar to that for tension specimens except that both sides should be repeatedly struck off smooth. It requires but a few minutes to measure a specimen by this apparatus.

Le Chatelier's Calipers.

Le Chatelier's calipers are shown in Fig. 97. This apparatus consists of a small split cylinder of spring brass or other suitable metal of 0.5 mm. (.0197-in.) in thickness, 30 mm. (1.1875-ins.) internal diameter, and 30 mm. high, forming the mold, to which on either side of the split are attached two indicators 165 mm. (6.5-ins.) long from the centre of the cylinder, with pointed ends A A, as shown upon the sketch.

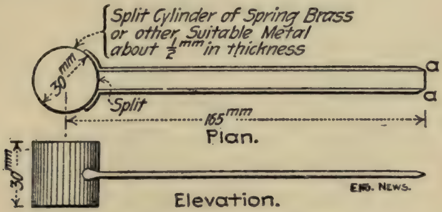

Fig. 97, Le Chatelier's Calipers.

This apparatus is used in determinating the soundness of cement in Great Britain, where the standard specifications[1] demand that the cement shall not show a greater expansion than 12 mm. after having been spread out for a depth of 3 inches and exposed to the air for 24 hours at a temperature of 58° to 64° F. The test is to be conducted as follows:

The mold is to be placed upon a small piece of glass and filled with cement gauged in the usual way, care being taken to keep the edges of the molds gently together while this operation is being performed. The mold is then covered with another glass plate, a small weight is placed on this and the mold is immediately placed in water at 58° to 64° F. and left there for 24 hours.

The distance separating the indicator points is then measured, and the mold placed in cold water, which is brought to a boiling point in 15 to 30 minutes, and kept boiling for six hours. After cooling, the distance between the points is again measured, the

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[1] Report—Committee on Cement, Engineering Standards Committee.

difference between the two measurements represents the expansion of the cement, which must not exceed the limits laid down in the specification.

OBSERVATIONS.

Importance of the Test.

The most important quality of cement is soundness, for no matter how high a degree of tensile strength a cement may develop at comparatively short periods, if it fails to resist the disintegrating influences of the atmosphere or the water in which it may be placed, it is useless as a material of construction. This tendency to disintegrate, fall to a powder, crack or expand on mixing the cement with water is termed "blowing." This fault is usually due to improper proportioning of the raw materials, allowing an excess of lime over what will combine with the silica and alumina of the cement mixture; or an improper burning, failing to raise the temperature to the point where all the lime may combine with the silica and alumina, thus leaving some in the uncombined state; or from insufficient grinding of the raw materials making it impossible for all the lime to come in contact with and unite with the silica and alumina. This free or loosely combined lime on coming in contact with water is slaked and expands, causing the cement to crack and fall to pieces.

Causes of Unsoundness.

Some discussion has been aroused of late as to what causes the failure of cement to stand the various tests for soundness. Some of the various compounds which may be present in cement, calcium di-silicate, alkalies, etc., are said to promote checking in the boiling test. All authorities seem to agree, however, that the chief cause is the presence of free or unstable lime over and above a certain limit. This free lime slacks *after* the cement has itself hardened or set, causing the test-piece to warp and check from the expansion set up by the change. The object of all tests for soundness is, therefore, to ascertain if the maximum of free lime that may safely be present has been exceeded.

A certain small percentage of free lime is present in all cement. I have frequently added as much as 5 per cent. of unslaked lime (prepared from precipitated calcium oxalate, and hence very finely pulverized) to cement, and yet pats made from the mixture passed both boiling and 28-day cold tests. If the lime is coarser, the quantity which can be added is much smaller. Slaked lime may be added in large quantities without affecting either boiling or cold water pats; so may also carbonate of lime. Pats with any proportion of either are perfectly sound.

Effect of Seasoning on Soundness.

Anything which promotes the changing over of the free lime into slaked lime or carbonate of lime will, therefore, cause cement at first unsound to become sound. The air always contains the elements, moisture and carbon dioxide, to bring about such a change, so that if cement that is unsound is stored for any length of time it will gradually become sound, from the slaking and carbonating of the free lime. This is illustrated by the following table:

TABLE XLI.—SHOWING EFFECT OF SEASONING ON SOUNDNESS.

Age in days after being ground.[1]	Cement No. 1.	Cement No. 2.	Cement No. 3.	Cement No. 4.	Cement No. 5.
	Results of 5 hour steam test (A. S. C. E.)				
0	Checked	Partly disintegrated	Checked	Checked	Entirely disintegrated
1	Checked	Badly Checked	Checked	O. K.	Entirely disintegrated
3	Slightly Checked	Badly Checked	Slightly Checked	......	Partly disintegrated
7	O. K.	Checked	Slightly Checked	......	Badly Checked
14	......	Checked	O. K.	......	Badly Checked
21	......	Slightly Checked	......	......	Checked
28	......	O. K.	......	......	Checked
90	......	......	......	......	O. K.

Cement which has seasoned sound is just as good as one which was sound when freshly made, and the writer does not think the

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[1] Samples were seasoned in a small paper bag on a shelf in the laboratory.

engineer need concern himself whether the manufacturer prefers to make cement which is sound when fresh, or whether he prefers to age it sound in his stock-house. So long as it is sound he is secure, and possibly the softer burned clinker, usually unsound when freshly ground, will grind with a greater percentage of flour, increasing the sand-carrying capacity of the cement.

Effect of Fine Grinding of the Raw Materials on Soundness.

In order for cement to stand the boiling test when fresh from the grinding mills, the raw materials must be finely ground. The unsoundness due to coarse grinding of the raw materials is probably the hardest form of unsoundness to cure by aging. This is particularly so if the clinker has been burned very hard, as the coarse pieces of limestone, calcined to free lime, are locked up in a case of clinker. If this case is not broken in grinding, the free lime is left surrounded by a wall of clinker and will be very slowly acted on by the moisture of the air. The experiment in Table XLII seems to prove this very thing. Laboratory records show the unsoundness of this sample to have been due to coarse grinding of the raw mixture. The fine particles passed to boiling test fresh, the coarse ones failed even on grinding, but on aging

TABLE XLII.—SHOWING EFFECT OF FINENESS OF GRINDING OF CLINKER ON SOUNDNESS.

Condition of Cement as Tested.	Fineness.		Result of 5 hours steam test. (A. S. C. E.)
	Residue No. 100.	Residue No. 200.	
As received from the mills, tested one day old	8.5	27.0	Partially disintegrated
As received from the mills, tested again after seasoning one week.	8.5	27.0	Partially disintegrated
As received from the mills, tested again after seasoning one month	8.5	27.0	Badly checked
Portion of sample passing No. 200 sieve, tested one day old	0.0	0.0	Sound
Sample ground to all pass a No. 200 sieve, tested one day old	0.0	0.0	Slightly checked
Sample ground to all pass a No. 200 sieve, tested one week after grinding	0.0	0.0	Sound

one week, the ground particles stood the test. Aging the cement, however, for two weeks failed to make it sound, because the free lime was locked up in the coarse particles, where hydration could only take place very slowly, but, on grinding the coarse particles, the air had a chance to get at the free lime and convert it to the innocuous hydroxide.[1]

Effect of Fine Grinding of Cement Itself on Soundness.

Fine grinding of the cement itself will, even without aging, often make it pass the boiling test. The reason for this is that the water used to gauge the pat can get at the lime to slake it before the cement sets. Table XLIII is given to illustrate this:

TABLE XLIII.—SHOWING EFFECT OF FINE GRINDING ON SOUNDNESS.

Cement No.	Results of 5 hour steam test A. S. C. E.)		
	As received.	Ground to pass No. 200.	Ground to an impalpable powder.
1	Checked	Sound	......
2	Checked	Sound	......
3	Checked	Slightly checked	Sound
4	Checked	Slightly checked	Sound

Effect of Sulphates on Soundness.

Pats allowed to harden in steam or hot water will often pass the boiling test where pats hardened in air will not. It must be remembered that checking is caused by slaking after the pats are fully hardened. If they are placed in steam to harden the moist air merely accelerates the slaking of the lime, doing the work before the pat hardens, just as heat hastens any chemical action. The addition of sulphates, either as gypsum or plaster of Paris, aids the cement in standing the boiling test, probably because it delays the set until after the lime has slaked. The rendering of the free lime inert by the formation of compounds with the lime by the gypsum seems hardly probable, since the lime and gypsum could not react unless both were in solution, and if the water

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[1] See also Taylor, Proceedings Am. Soc. Test. Mat., III., (1903), 377, and Butler, Portland Cement, p. 174.

could get at the free lime to dissolve it, slaking would take place on adding water only, and the harmless hydroxide would be formed. The early hardness due to gypsum can hardly play any part, since cements breaking as high as 600 pounds in 24 hours may fail on the boiling test, while briquettes breaking at 150 pounds may be sound. My own experiments go to show that anything which will delay the setting of cement until after the free lime has slaked, or that will hasten the slaking of the free lime before the pat sets, will make cement sound. The table given below shows the effect of additions of plaster on the boiling test:

TABLE XLIV SHOWING EFFECT OF ADDITIONS OF GYPSUM OR PLASTER OF PARIS ON SOUNDNESS.

Sample.	Per cent. SO_3	Result of 5 hour steam test (A. S. C. E.)[1]			
		0.5 Per cent. Plaster added.	1.0 Per cent. Plaster added.	2.0 Per cent. Plaster added.	3.0 Per cent. Plaster added.
Cement......	1.21	Sound	......	......	......
Cement......	1.43	Checked	Sound	......	......
Cement......	1.18	Checked	Checked	Sound	......
Cement......	1.36	Checked	Checked	Checked	Sound
Ground clinker	0.31	Checked	Checked	Sound	......

Value of Accelerated Tests.

At the 1903 meeting of the American Society for Testing Materials Mr. W. P. Taylor, of the Philadelphia Testing Laboratory, read a very carefully prepared paper upon the boiling test[2] in which he compared the results of neat briquettes and neat pats with the results of the boiling test. As is usual, he considered a falling off of the strength of neat briquettes on long time tests and a cracking and warping of the neat cold water pat as being positive evidence of the presence of injurious constituents in the cement. He gives these figures: "Of all the samples failing to pass the boiling test 34 per cent. of them developed checking or curvature in the normal pats or a loss of strength in less than 28 days. Of those samples that failed in the boiling test but re-

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[1] All samples were unsound without addition of plaster of Paris.

[2] Proceedings Amer. Soc. Test. Mat , III., (1903), 374.

mained sound for 28 days, 3 per cent. of the normal pats showed checking or abnormal curvature in 2 months, 7 per cent. in 3 months, 10 per cent. in 4 months, 26 per cent. in 6 months, and 48 per cent. in one year; and of these same samples 37 per cent. showed a falling off in tensile strength in 2 months, 39 per cent. in 3 months, 52 per cent. in 4 months, 63 per cent. in 6 months, and 71 per cent. in one year. Or taking all these together, of all the samples that failed in the boiling test 86 per cent. of them gave evidence in less than a year's time of possessing some injurious quality.

"On the other hand, of those cements passing the boiling test but one-half of 1 per cent. gave signs of failure in the normal pat tests and but 13 per cent. showed a falling off in strength in a year's time."

It is unfortunate that the test which seems to be accepted by the majority as a standard is the long-time cold-water pat, a test requiring such length of time for its completion as to practically forbid its use. The conditions of the case demand a rapid test in order that the consumer may not be required to store the cement for a long period of time while he awaits the results of his cold-water pats.

To the manufacturer the steam and boiling tests are exceedingly useful, for if a cement will pass these tests it will pass any test to which it may be subjected. He can not hold his cement in his stock-house for months while he ascertains if it will pass the cold-water pat test and so he applies an accelerated test to tell him if this cement will pass the tests to which it is likely to be put. To my mind there is a strong comparison between the steam test and the color test for carbon, so much used in the steel works laboratories. While this latter test is very useful to the manufacturer still no engineer would condemn steel on the result of such a test, for though it may give correct results in nine out of ten cases he does not care to take the risk of this being the tenth case and of throwing out a good steel, and so working great hardship to the manufacturer.

Unquestionably much good concrete has been made from so-called unsound cement, and this is the key to the whole objection to the hot test. It is probable that much of the first American Portland cement would not have passed the steam test, yet it is upon the merits of the work done with this cement that engineers are now using American instead of imported cement. Butler gives a strong plea for the Faija test and states that in the twenty years this test has been in use, no cases of failure in work by cement passing this test have come under his observation. If the Faija test is severe enough to exclude all bad cements, then the boiling test is needlessly severe as it rejects many cements which pass Faija's test.

All cement probably contains some free lime. From the nature of the case this must be so, since cement raw materials are not ground to a degree of fineness nor carried to a state of fusion which would permit of every molecule of lime coming in contact with a molecule of silica or of alumina. Now there are limits beyond which if the uncombined or free lime goes, certain results will take place. Let us suppose that with a very small percentage present the cement will fail on the boiling test but pass satisfactorily five hours in steam, and if a still larger percentage is present it will fail in the steam but pass the Faija test. Now, again, let us suppose that a neat mixture with a certain small percentage of free lime is sound, with a larger percentage a 3:1 sand mixture is sound, with a still larger percentage a 1:3:8 concrete is sound. (It is well understood that the tendency of cement to disintegrate is greater in a neat paste than in a sand mixture, and anyone with experience in cement testing knows of cases where neat briquettes were disintegrated in time and yet the sand ones were sound and strong). Now how do we know that the limit of lime which may be present in good cement (that is cement which will make enduring concrete) is coincident with that maximum which may be present for a sound boiling test?

Nearly all advocates of the steam test have tried to prove these two limits coincident by comparing the steam test with the results of neat pats and neat briquettes. Usually the coincidence of a failure on the boiling test with either a warping or cracking of the neat pats or a loss of strength in the neat briquettes on long time tests is considered competent evidence in favor of the boiling test. In reality cement is seldom used neat. A cement which fails on the boiling test, whose neat briquettes fall off in strength after 7 or 28 days, yet whose sand briquettes increase in strength as they grow older, has certainly given evidence that it will make good concrete. In weighing evidence for any test it must be remembered that we do not make the soundness test to see if neat briquettes will fail in strength as they age or if neat pats will warp and decay, but whether sidewalks, piers, abutments, foundations, walls, floors and buildings of concrete, not neat cement, will be permanent, and the thing therefore to compare the boiling test with, is concrete. Not until we can compare our laboratory records with many examples of both failures and successes in actual work will we have reliable data for forming our conclusions as to the reliability of the various tests for soundness.

Experiments made by a committee of the Society of German Portland Cement Manufacturers in connection with the Royal Testing Laboratory at Charlottenburg forced them to report in 1900 and again in 1903 that none of the so-called accelerated tests for consistency of volume was adapted to furnish a reliable and quick judgment in all cases concerning the applicability of a cement. The experiments which they made consisted in putting the cement into actual work and observing it during a period of four years. The committee recommended the 28-day cold water pat as a standard test. If this test is taken as a standard the hot test will reject two good cements for every bad one.

MISCELLANEOUS.

CHAPTER XVIII.

THE DETECTION OF ADULTERATION IN PORTLAND CEMENT.

Cements are adulterated with natural cement, blast-furnace slag, ground limestone, shale, ashes, etc. Some of these substances are so similar to Portland cement that chemical analysis fails to show their presence. It is, therefore, necessary to direct special tests to their detection. When present in small quantities, it is probable that even such tests will fail to show positively an adulterated cement.

Tests of Drs. R. and W. Fresenius.

Drs. R. and W. Fresenius,[1] at the request of the Association of German Cement Manufacturers, made investigations into the subject of cement adulteration looking to a method of detecting the same. They experimented upon twelve samples of pure Portland cement from Germany, England and France, and compared the results of tests upon these with the results obtained by similar tests upon three kinds of hydraulic lime, three kinds of weathered slag, and two of ground slag. The cements were of various ages and had been exposed to the air for various lengths of time. On the next page are tabulated their experiments for comparison.

Proposed Tests.

As the result of these experiments they proposed the following tests for the detection of adulteration:

1. The specific gravity.

This must not be lower than 3.10.

2. The loss on ignition.

This should be between 0.3 and 2.59 per cent.; certainly not much more.

3. The alkalinity imparted to water. 0.5 gram of cement

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[1] *Ztschr. anal. Chem.*, **23**, 175, and **24**, 66.

should not render 50 cc. of water so alkaline as to require more than 6.25 cc. nor less than 4 cc. of decinormal acid to neutralize.

4. The volume of normal acid neutralized.

One gram of cement should neutralize from 18.8 to 21.7 cc. of normal acid.

5. The volume of potassium permanganate reduced.

One gram of cement should reduce not much more than 0.0028 gram of potassium permanganate.

TABLE XLV.—ADULTERATION IN PORTLAND CEMENT.

Description.	1 Specific gravity.	2 Loss on ignition. Per cent.	3 Alkalinity imparted to water by 0.5 gram. cc. of decinormal acid.	4 Volume of normal acid neutralized by 1 gram. cc.	5 Weight of $KMnO_4$ reduced by 1 gram. mg.	Weight of CO_2 absorbed by 3 grams. mg.
Portland cement, A...	3.155	1.58	6.25	20.71	0.79	1.4
“ “ B...	3.125	2.59	4.62	21.50	2.38	1.6
“ “ C...	3.155	2.11	4.50	20.28	0.93	1.8
“ “ D...	3.144	1.98	5.10	21.67	1.12	1.0
“ “ E...	3.144	1.25	6.12	19.60	0.98	1.6
“ “ F...	3.134	2.04	4.95	20.72	1.21	1.1
“ “ G...	3.144	0.71	4.30	22.20	0.89	0.0
“ “ H...	3.125	1.11	4.29	20.30	1.07	0.7
“ “ J...	3.134	1.00	4.00	19.40	2.01	0.0
“ “ K...	3.144	0.34	4.21	20.70	0.98	0.0
“ “ L...	3.154	1.49	4.60	18.80	2.80	0.3
“ “ M...	3.125	1.25	5.50	20.70	2.33	0.0
Hydraulic lime A...	2.441	18.26	20.23	21.35	1.40	27.8
“ “ B...	2.551	17.82	22.73	26.80	0.93	31.3
“ “ C...	2.520	19.60	19.72	19.96	0.98	47.7
Weathered slag A...	3.012	0.76	0.91	14.19	74.60	3.6
“ “ B...	3.003	1.92	0.70	13.67	60.67	3.5
“ “ C...	2.967	1.11	1.00	9.70	44.34	2.9
Ground slag I...	3.003	0.32	0.31	3.60	64.40	2.4
“ “ II...	2.873	0.43	0.11	8.20	73.27	2.2

6. The weight of carbon dioxide absorbed.

Three grams of cement should not absorb more than 0.0018 gram of carbon dioxide.

The tests 1, 3, 4, and 5 are for the detection of slag and 1, 2, 3 and 6 for the detection of hydraulic lime.

Drs. R. and W. Fresenius also tried these tests upon experimental mixtures containing 10 per cent. of slag or hydraulic lime, and in each case were able to detect the impurity.

Carrying Out the Tests.

The methods employed for carrying out the tests were as follows:

1. They used for taking the specific gravity the method of Schumann (see page 280), with turpentine as the liquid. The end of the tube was corked to prevent evaporation, the temperature kept constant, and the vessel carefully shaken to displace air bubbles.

2. For loss on ignition 2 grams of cement were weighed into a tared crucible, and then heated over a Bunsen burner for twenty minutes. The loss shown on again weighing was the loss on ignition.

3. For the "alkalinity to water test." The substance was finely powdered and passed through a sieve of 5,000 meshes to the square centimeter.[1] Of the resulting powder, 1 gram was shaken up with 100 cc. of distilled water without warming for ten minutes. The solution was then passed through a dry filter paper into a dry vessel and 50 cc. of the filtrate titrated with decinormal hydrochloric acid.[2]

4. For "standard acid necessary to decompose." One gram of the fine powder obtained in 3 was shaken with 30 cc. of normal hydrochloric acid[3] and 70 cc. of water for ten minutes, without warming, and filtered through a dry filter paper 50 cc. of the filtrate were then titrated with normal caustic soda.[4]

5. For the volume of permanganate reduced. One gram of the fine powder, obtained in 3, was treated with a mixture of 50 cc. of dilute sulphuric acid (sp. gr. 1.12) and 100 cc. of water.

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[1] 32,260 meshes to the square inch.

[2] To make decinormal hydrochloric acid, refer to page 233, with the notes under this section, and taking such a quantity of dilute hydrochloric acid as contains 3.65 grams of HCl, dilute this volume to 1 liter. Check its value by one of the methods given in the section referred to. The $^2/_5$ N nitric acid may be diluted to $^1/_{10}$ N strength and used in place of the $^1/_{10}$ N hydrochloric acid.

[3] Normal acid should contain 36.5 grams HCL per liter.

[4] To prepare normal caustic soda, refer to page 232, and using the above normal acid as a standard proceed as directed there. The $^2/_5$ N solutions used in checking the per cent. of lime in cement mixture (see page 232) may be used for this test. In this case shake up the cement with a mixture of 75 cc. of $^2/_5$ normal acid and 25 cc. of water, and titrate back with the $^2/_5$ normal alkali.

The resulting solution was then titrated with potassium permanganate solution.[1]

6. For carbon dioxide absorbed, about 3 grams of the fine powder obtained as in 3, were placed in a weighed tube and a stream of carbon dioxide allowed to pass over it. The sample was then dried in a desiccator over sulphuric acid (sp. gr. 1.184) and weighed. The increase in weight gave the amount of carbon dioxide absorbed, a small calcium chloride drying tube was placed after the tube containing the cement to absorb any water evolved.

Le Chatelier's Test.

Le Chatelier has devised a very neat test for the adulteration in cement, depending upon the lower density of the adulterant than of the cement. His method consists in separating these lighter impurities from the cement by means of a heavy liquid, a mixture of methyl iodide and benzene, prepared of such strength that they float upon its surface while the pure Portland sinks to the bottom.

This method is in use in the Philadelphia City Testing Laboratory and gives good satisfaction there, where it is used to detect additions of Rosendale to Portland cement.[2]

Preparation of the Heavy Liquid.

As the first step the methyl iodide solution must be prepared. This should be of density 2.95 according to Le Chatelier. As the density of the methyl iodide itself is 3.1, benzene must be added in small quantities until a crystal of aragonite (serving as a guide) whose density is 2.94 just remains at the surface. Since very small quantities of benzene change the density of the methyl iodide considerably it is well to make two solutions, one a little above and one a little below the density sought, and then to add the one to the other until the required density is obtained. By this means a more gradual change is affected and the danger of over-running the mark is lessened.

Apparatus.

Le Chatelier used in his experiments a little glass tube 10 mm.

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[1] Dissolve 0.28 gram of $KMnO_4$ in 100 cc. of water. Not much more than 1 cc. of this solution, or 2 cc. of the solution used to determine ferric oxide in cement should be required if the cement is unadulterated.

[2] Taylor, *Chem. Eng.*, I., 258.

in diameter and 70 mm. long. The tube (Fig. 98) is widened at the top to a funnel and drawn at the bottom with a regular slope to an opening of 1 mm. diameter. This opening is closed on the interior a little above the bottom by a plunger consisting of a small emery ground-glass stopper on the end of a glass rod which projects above the funnel top.

Fig 98. Separatory Funnel for Methyl Iodide Solutions.

Test.

To make a test the stopper is wet with water to make a tight joint and inserted into the opening of the tube. Grease cannot be used as it is dissolved by the methyl iodide solution. Ten grams of the suspected cement are weighed into the tube and 5 cc. of methyl iodide solution (sp. gr. 2.95), prepared as above, poured upon it. A thin platinum wire bent into a loop around the plunger is then moved around and up and down in the liquid in a lively manner in order to drive out all air bubbles and mix the cement and liquid thoroughly. The apparatus is now set aside for an hour, when it will be found that the slag is on top and the cement below. The apparatus is now placed over a dry filter, the stopper raised and the cement and part of the liquid allowed to run out. The cement is retained upon the filter while the liquid is caught in a vessel below and may be used again. The slag and the rest of the liquid are then run out upon another filter, and the excess of liquid caught in a vessel for use again. The filters containing the slag and cement are washed with benzene, dried and weighed separately. From the weights the percentage of adulteration can be calculated. The slag and cement can then be analyzed chemically, if thought necessary, as a further guide.

Microscopic Test.

The microscope furnishes us with a very good means of detecting added material in cement. Butler[1] recommends that those particles which pass a 76 sieve and are retained upon a 120 sieve be examined with a low power (say one-inch) objective. The particles of pure, well-burned cement clinker of this size will then appear dark, almost black in color, resembling coke somewhat, and will possess the characteristic spongy honey-combed appearance of cement clinker. The particles of less well-burned clinker, always present in cement, will, when examined in the same way, present the same shape and structure, but will differ in color, being light brown and semi-transparent, resembling gum arabic. Intermediate products range from black to light brown. These particles are always of a more or less rounded nature. Particles of slag of the same size viewed under the same conditions differ somewhat in color, according to the nature of the slag. Usually the particles are light colored, of angular fracture, and instead of the particles presenting a rounded appearance the edges are sharp like flint. Not to be mistaken for the slag, however, are the particles of pebbles from the tube-mills used to grind the clinker. These latter may be distinguished from the slag by picking out the particles in question with a pair of pincers, crushing them in a small agate mortar and treating them with hydrochloric acid. The slag is readily attacked while the débris from the pebbles is not attacked. Particles of iron from the crushers are also present in the residue caught upon the 120 sieve. These may be identified by their black metallic appearance and their behavior with the magnet. Neither of these can, of course, be considered as adulterants. Limestone and cement rock if present are in more or less flattened particles, and the latter is always dark gray in color. Both of these may be readily detected by effervescence with dilute acids. The foreign particles may also be picked out of the residue with a pair of tweezers, ground finely and identified by chemical analysis.

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[1] "*Portland Cement*," p. 273.

CHAPTER XIX.

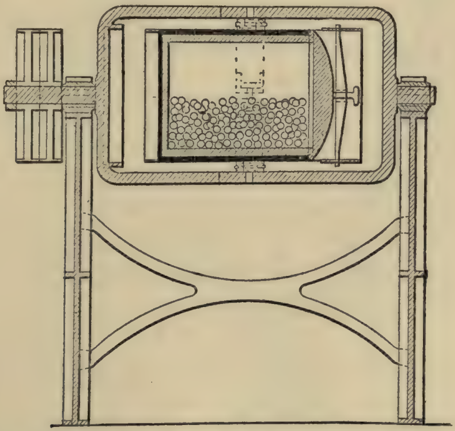
TRIAL BURNINGS.

In prospecting new deposits of raw materials, it is often thought advisable to make up small trial lots of cement in the laboratory and examine into the physical properties of these. For such trials, it is necessary to crush the raw materials, if they are not already in small pieces, and correctly proportion them. The mixture is then finely ground, the powder moistened with water and moulded into little cubes or balls and these latter are burned in some form of laboratory kiln. The resulting clinker is then sorted to separate out the under-burned and the hard-burned portions are ground to the same degree of fineness as commercial cement. It is also often desirable to make experimental burnings in the investigation of the various problems which arise in connection with the manufacture and properties of cement. The apparatus described below is suitable for such purposes and has been used in similar work by various investigators.

For crushing the raw rock small Blake or Bosworth crushers such as are used in almost all laboratories for crushing ores will be found convenient. These can be so adjusted as to crush the rock to about wheat size and finer. They can be obtained either hand or power driven, but for the work indicated above they should be power driven and attached to a shafting somewhere about the mill or run by an independent motor. After crushing the materials to the size indicated above they should be carefully analyzed and mixed in the proper proportions (see Chapter IV). The mixture should then be finely ground. The degree of fineness should be indicated by the nature of the investigation. If a test is being made of the suitability of certain raw materials the mixture should be ground no finer than it would be in actual mill practice, or about 95 per cent. through a 100 mesh sieve.

Samples of clay and marl should be thoroughly dried before analyzing and proportioning them. This can be done over a hot plate or steam radiator, etc.

For finely grinding the mixture, a jar mill will be found as convenient as anything else. Fig. 99 shows the form (made by the Abbé Engineering Co.) which the writer has used in his laboratory and found very satisfactary. This consists of a porcelain jar, the cover of which is fastened tightly on by means of a clamp, as shown. The jar itself is held in a revolving frame by brass bands, one of which can be loosened by means of a thumb screw, allowing the jar to be removed from the frame. The jar is filled half full of porcelain balls and as the former revolves the material is ground by the latter. The jar is intended to make from 40 to 50 revolutions per minute and will grind about 15 pounds of material at a charge.



COPYRIGHT, 1904, BY ABBÉ ENGINEERING CO.

Fig. 99, Jar Mill.

After grinding finely, the powder is mixed with water until it is plastic and then moulded into small cubes or balls. The writer has usually found it an excellent plan to roll the mass out in a thin sheet on a pane of glass and then cut this into thin strips with the point of a spatula or trowel. These strips on drying usually break up at right angles into small cubes. If they do not, the breaking can then be done by hand. The size of the balls or cubes will depend upon the size of the furnace—a small furnace will require a smaller ball than a larger one. They should not, however, be smaller than a pea for even a small furnace.

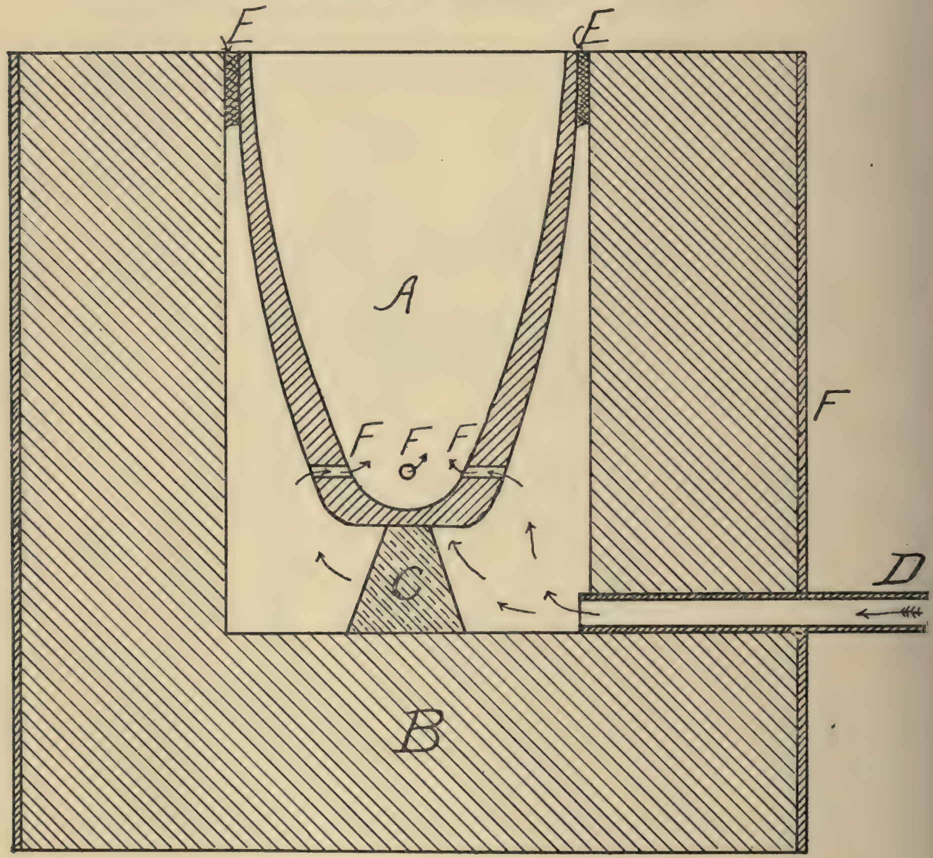


Fig. 100, Furnace for Experimental Burnings.

For burning small quantities of cement the writer has found the form of kiln shown in Fig. 100 useful. It consists of a large Battersea crucible (size R) 13 inches in height and 10 inches in diameter, resting on a piece of fire-brick, C, and fitting snugly into a cylinder of concrete, B. The crucible is punched with four holes F, F, F, F, around its bottom and through these the air for cumbustion enters the crucible. A tight joint between the crucible and the concrete cylinder is made by means of fire-clay or wet asbestos as shown at E, E. Air is brought into the concrete cylinder by means of the pipe D. F, F, is a sheet iron jacket surrounding the cylinder of concrete. The walls of the cylinder are about 6 inches thick. Air for burning may be obtained from a compressor or a small Root or Crowell blower. Larger crucibles than the size indicated can be obtained when a larger furnace is needed. The one given above will burn 3 or 4 pounds of cement. Charcoal or oil coke is used as a fuel. A small piece of cotton waste saturated with oil is placed in the crucible and when this is burning a few handfulls of charcoal are added and the air blast turned on. As soon as the charcoal is burned and the crucible is heated up, it is filled half full of charcoal and the little balls of slurry are added in a thin layer. More charcoal is placed over this and then more slurry, etc., until the crucible is full. A pair of fire bricks having an inch channel cut in one side of each is then placed over the crucible to form a cover and the heating continued until all the charcoal is burned away. The air is left turned on to cool the clinker after which the latter is sorted.

For research work when contamination with the fuel ash is objectionable, a small Fletcher furnace lined with a mixture of 90 parts coarse, burned magnesite and 10 parts Portland cement will be found useful.

Bleininger describes[1] a kiln used in the Ohio State University Ceramic Department. This consists of a straight shaft of fire-brick with walls 4 inches thick, divided into three distinct divisions. Air is forced into a space 4 inches high at the bottom under a pressure of about 12 ounces from a blower through a 2-inch pipe. This space is divided from the next division by means of a cast-iron plate provided with concentric rows of holes. Above this plate about 5 inches away from it an iron pan is supported by two bricks. Petroleum is fed into this pan by means of a ¼-inch pipe, running in by gravity from a can some distance away. Several inches above the pan the

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[1] Ohio Geol. Survey, Bul. No. 3 [IV.] Manufacture of Hydraulic Cements.

whole cross-section of the shaft is filled with broken fire-brick. Above this compartment the third compartment is formed by a grating of bricks, made of a mixture of 80 per cent. magnesite and 20 per cent. Portland cement. On this grating the balls of cement mixture are heaped up to the top of the compartment, which is about 8 inches high. The cover consists of a perforated clay tile upon which are piled broken bricks. The clinker compartment is accessible from the outside by means of a door which is closed by a fire-brick plug which can be removed and the clinkers withdrawn and examined.

To start the furnace, a small amount of paper and wood is placed upon the pan through a hole provided for this purpose. The oil on coming in contact with the hot pan is vaporized and mixes with the air in the compartment filled with broken brick. The time required for a burn in this kiln is about two hours. By removing the pan bricks and broken pieces of brick this kiln can also be used for burning with coke.

When large quantities of cement are to be burned a small shaft kiln made of fire-brick and provided with grate bars can be used. The cement mixture and coke being charged in alternate layers after the furnace is well heated up and a bed of hot coals is obtained on the grate bars. The temperature of such a kiln can be greatly increased by providing means of blowing air through the grate bars.

Prof. E. D. Campbell, of the University of Michigan, used in his experimental work a small rotary kiln consisting of an iron pipe, 8 inches in diameter and 32 inches long. This was lined with four sections of hard burned magnesite pipe, 3 inches internal diameter, and was revolved by means of a ½-horse-power motor, at a speed of one revolution in 85 seconds. It was fired by means of a Hoskins gasoline burner under an air pressure of 50 pounds.

After sorting the clinker it is crushed and ground in the jar mill mentioned before, the degree of fineness being regulated by conditions. Plaster or gypsum must, of course, be added to slow the set of the resulting cement and may be ground in with the clinker.

APPENDIX.

TABLES.

TABLE XLVI.—THE ATOMIC WEIGHTS OF THE MORE IMPORTANT ELEMENTS. $O = 16$.

Name	Symbol	Weight	Name	Symbol	Weight
Aluminum	Al	27.1	Iron	Fe	55.9
Antimony	Sb	120.2	Lead	Pb	206.9
Arsenic	As	75.0	Magnesium	Mg	24.36
Barium	Ba	137.4	Manganese	Mn	55.0
Bismuth	Bi	208.5	Mercury	Hg	200.0
Boron	B	11.0	Nickel	Ni	58.7
Bromine	Br	79.96	Nitrogen	N	14.04
Cadmium	Cd	112.4	Oxygen	O	16.0
Calcium	Ca	40.1	Phosphorus	P	31.0
Carbon	C	12.0	Platinum	Pt	194.8
Chlorine	Cl	35.45	Potassium	K	39.15
Chromium	Ch	52.1	Silicon	Si	28.4
Cobalt	Co	59.0	Silver	Ag	107.93
Copper	Cu	63.6	Sodium	Na	23.05
Fluorine	F	19.0	Strontium	Sr	87.6
Gold	Au	197.2	Sulphur	S	32.06
Hydrogen	H	1.008	Tin	Sn	119.0
Iodine	I	126.97	Zinc	Zn	65.4

TABLE XLVII.—FACTORS.

Found.	Sought.	Factor.	Found.	Sought.	Factor.
CdS	CaS	0.50000	$Mg_2P_2O_7$	MgO	0.36190
CaO	$CaCO_3$	1.7847	$Mg_2P_2O_7$	$MgCO_3$	0.75722
$CaSO_4$	CaO	0.41185	$Mg_2P_2O_7$	P_2O_5	0.63809
$CaSO_4$	$CaCO_3$	0.73504	K_2PtCl_6	K_2O	0.19398
CaS	$CaSO_4$	1.8872	K_2PtCl_6	KCl	0.53076
CO_2	C	0.27272	$BaSO_4$	S	0.13734
CO_2	$CaCO_3$	2.2743	$BaSO_4$	SO_3	0.34291
CO_2	$MgCO_3$	1.9154	$BaSO_4$	H_2SO_4	0.42006
$AgCl$	HCl	0.25424	$BaSO_4$	$CaSO_4$	0.58565
Fe	Fe_2O_3	1.4284	$BaSO_4$	$(CaSO_4)_2H_2O$	0.62184
Fe	FeO	1.2856	$BaSO_4$	$CaSO_4 \cdot 2H_2O$	0.73750
Fe_2O_3	FeO	0.70007	$BaSO_4$	CaS	0.30895

TABLE XLVIII.—FOR CONVERTING $Mg_2P_2O_7$ TO MgO.

Percentage of MgO. 0.5 gram sample.	Grams of $Mg_2P_2O_7$ weighed.									
	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
1.00 . . .	.0138	.0139	.0141	.0142	.0144	.0145	.0146	.0148	.0149	.0151
1.10 . . .	.0152	.0153	.0155	.0156	.0158	.0159	.0160	.0162	.0163	.0164
1.20 . . .	.0166	.0167	.0168	.0170	.0171	.0173	.0174	.0175	.0177	.0178
1.30 . . .	.0180	.0181	.0182	.0184	.0185	0.186	.0188	.0189	.0191	.0192
1.40 . . .	.0193	.0195	.0196	.0197	.0199	.0200	.0202	.0203	.0204	.0206
1.50 . . .	.0207	.0209	.0210	.0211	.0213	.0214	.0215	.0217	.0218	.0220
1.60 . . .	.0221	.0222	.0224	.0225	.0226	.0228	.0229	.0231	.0232	.0233
1.70 . . .	.0235	.0236	.0238	.0239	.0240	.0242	.0243	.0244	.0246	.0247
1.80 . . .	.0249	.0250	.0251	.0253	.0254	.0255	.0257	.0258	.0260	.0261
1.90 . . .	.0262	.0264	.0265	.0267	.0268	.0269	.0271	.0272	.0273	.0275
2.00 . . .	.0276	.0278	.0279	.0280	.0282	.0283	.0285	.0286	.0287	.0289
2.10 . . .	.0290	.0291	.0293	.0294	.0296	.0297	.0298	.0300	.0301	.0302
2.20 . . .	.0304	.0305	.0307	.0308	.0309	.0311	.0312	.0314	.0315	.0316
2.30 . . .	.0318	.0319	.0320	.0322	.0323	.0325	.0326	.0328	.0329	.0330
2.40 . . .	.0331	.0333	.0334	.0336	.0337	.0338	.0340	.0341	.0343	.0344
2.50 . . .	.0345	.0347	.0348	.0349	.0351	.0352	.0354	.0355	.0356	.0358
2.60 . . .	.0359	.0360	.0362	.0363	.0365	.0366	.0367	.0369	.0370	.0372
2.70 . . .	.0373	.0374	.0376	.0377	.0378	.0380	.0381	.0383	.0384	.0385
2.80 . . .	.0387	.0388	.0389	.0391	.0392	.0394	.0395	.0396	.0398	.0399
2.90 . . .	.0400	.0402	.0403	.0405	.0406	.0407	.0409	.0410	.0412	.0413
3.00 . . .	.0414	.0416	.0417	.0419	.0420	.0421	.0423	.0424	.0425	.0427
3.10 . . .	.0428	.0429	.0431	.0432	.0434	.0435	.0436	.0438	.0439	.0441
3.20 . . .	.0442	.0443	.0445	.0446	.0447	.0449	.0450	.0452	.0453	.0454
3.30 . . .	.0456	.0457	.0458	.0460	.0461	.0463	.0464	0.465	.0467	.0468
3.40 . . .	0.470	.0471	.0472	.0474	.0475	.0477	.0478	.0479	.0481	.0482
3.50 . . .	.0483	.0485	.0486	.0488	.0489	.0490	.0492	.0493	.0495	.0497

TABLE XLIX.—FOR CALCULATING THE PERCENTAGE OF LIME OR CARBONATE OF LIME WITH ONE-HALF GRAM SAMPLE.[1]

	55.0 C. C.			55.1 C. C.			55.2 C. C.	
	CaO	$CaCO_3$		CaO	$CaCO_3$		CaO	$CaCO_3$
1	1.018	1.816	1	1.016	1.814	1	1.015	1.812
2	2.036	3.632	2	2.032	3.628	2	2.030	3.624
3	3.054	5.448	3	3.048	5.442	3	3.045	5.436
4	4.072	7.264	4	4.064	7.256	4	4.060	7.248
5	5.090	9.080	5	5.080	9.070	5	5.075	9.060
6	6.108	10.896	6	6.096	10.884	6	6.090	10.872
7	7.126	12.712	7	7.112	12.698	7	7.105	12.684
8	8.144	14.528	8	8.128	14.512	8	8.120	14.496
9	9.162	16.344	9	9.144	16.326	9	9.135	16.308

[1] *Chemical Engineer*, I., 42.

TABLE XLIX.—(*Continued*).

55.3 C. C.

	CaO	$CaCO_3$
1	1.013	1.808
2	2.026	3.616
3	3.039	5.424
4	4.052	7.232
5	5.065	9.040
6	6.078	10.848
7	7.091	12.656
8	8.104	14.464
9	9.117	16.272

55.4 C. C.

	CaO	$CaCO_3$
1	1.011	1.805
2	2.022	3.610
3	3.033	5.415
4	4.044	7.220
5	5.055	9.025
6	6.066	10.830
7	7.077	12.635
8	8.088	14.440
9	9.099	16.245

55.5 C. C.

	CaO	$CaCO_3$
1	1.009	1.801
2	2.018	3.602
3	3.027	5.403
4	4.036	7.204
5	5.045	9.005
6	6.054	10.806
7	7.063	12.607
8	8.072	14.408
9	9.081	16.209

55.6 C. C.

	CaO	$CaCO_3$
1	1.007	1.797
2	2.014	3.594
3	3.021	5.391
4	4.028	7.188
5	5.035	8.985
6	6.042	10.782
7	7.049	12.579
8	8.056	14.376
9	9.063	16.173

55.7 C. C.

	CaO	$CaCO_4$
1	1.005	1.794
2	2.010	3.588
3	3.015	5.382
4	4.020	7.176
5	5.025	8.970
6	6.030	10.764
7	7.035	12.558
8	8.040	14.352
9	9.045	16.146

55.8 C. C.

	CaO	$CaCO_3$
1	1.004	1.792
2	2.008	3.584
3	3.012	5.376
4	4.010	7.168
5	5.020	8.960
6	6.024	10.752
7	7.028	12.544
8	8.032	14.336
9	9.036	16.128

55.9 C. C.

	CaO	$CaCO_3$
1	1.002	1.789
2	2.004	3.578
3	3.006	5.367
4	4.008	7.156
5	5.010	8.945
6	6.012	10.734
7	7.014	12.523
8	8.016	14.312
9	9.018	16.101

56.0 C. C.

	CaO	$CaCO_3$
1	1.000	1.785
2	2.000	3.570
3	3.000	5.355
4	4.000	7.140
5	5.000	8.925
6	6.000	10.710
7	7.000	12.495
8	8.000	14.280
9	9.000	16.065

56.1 C. C.

	CaO	$CaCO_3$
1	0.998	1.782
2	1.996	3.564
3	2.995	5.346
4	3.993	7.128
5	4.991	8.910
6	5.989	10.692
7	6.987	12.474
8	7.986	14.256
9	8.984	16.038

56.2 C. C.

	CaO	$CaCO_3$
1	0.996	1.779
2	1.992	3.558
3	2.988	5.337
4	3.984	7.116
5	4.980	8.895
6	5.976	10.674
7	6.972	12.453
8	7.968	14.232
9	8.964	16.011

56.3 C. C.

	CaO	$CaCO_3$
1	0.995	1.776
2	1.990	3.552
3	2.985	5.328
4	3.980	7.104
5	4.975	8.880
6	5.970	10.656
7	6.965	12.432
8	7.960	14.208
9	8.955	15.984

56.4 C. C.

	CaO	$CaCO_3$
1	0.993	1.773
2	1.986	3.546
3	2.979	5.319
4	3.972	7.092
5	4.965	8.865
6	5.958	10.638
7	6.951	12.411
8	7.944	14.184
9	8.937	15.957

TABLE XLIX.—(*Continued*).

	56.5 C. C.			56.6 C. C.			56.7 C. C.	
	CaO	$CaCO_3$		CaO	$CaCO_3$		CaO	$CaCO_3$
1	0.991	1.770	1	0.989	1.767	1	0.988	1.764
2	1.982	3.540	2	1.978	3.534	2	1.976	3.528
3	2.973	5.310	3	2.967	5.301	3	2.964	5.292
4	3.964	7.080	4	3.956	7.068	4	3.952	7.056
5	4.955	8.850	5	4.945	8.835	5	4.940	8.820
6	5.946	10.620	6	5.934	10.602	6	5.928	10.584
7	6.937	12.390	7	6.923	12.369	7	6.916	12.348
8	7.928	14.160	8	7.912	14.136	8	7.904	14.112
9	8.919	15.930	9	8.901	15.903	9	8.892	15.876

	56.8 C. C.			56.9 C. C.			57.0 C. C.	
	CaO	$CaCO_3$		CaO	$CaCO_3$		CaO	$CaCO_3$
1	0.986	1.761	1	0.984	1.757	1	0.983	1.754
2	1.972	3.522	2	1.968	3.514	2	1.966	3.508
3	2.958	5.283	3	2.952	5.271	3	2.949	5.262
4	3.944	7.044	4	3.936	7.028	4	3.932	7.016
5	4.930	8.805	5	4.920	8.785	5	4.915	8.770
6	5.916	10.566	6	5.904	10.542	6	5.898	10.524
7	6.902	12.327	7	6.888	12.299	7	6.881	12.278
8	7.888	14.088	8	7.872	14.056	8	7.864	14.032
9	8.874	15.849	9	8.856	15.813	9	8.847	15.786

The first column of each table gives the number of cubic centimeters of permanganate required by 0.5 gram of calcite (see page 186), and the second and third columns show the corresponding percentages of calcium oxide and calcium carbonate respectively where a half gram sample has been taken.

Example of the use of tables.—Suppose 0.5 gram of calcite takes 55.6 C. C. of permanganate, then write the values found in the table headed 55.6 C. C. on a card and stand near the burette table. The writer usually notes the CaO values in red ink and the $CaCO_3$ in black to avoid confusing them.

Now suppose we analyze a limestone and find it requires 51.3 C. C. then the percentage of lime and carbonate of lime may be calculated from the table as follows :

			CaO	$CaCO_3$
50.0	C. C.	=	50.35	89.85
1.0	C. C.	=	1.007	1.797
.3	C. C.	=	.3021	.5391
51.3			51.6591	92.1861

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